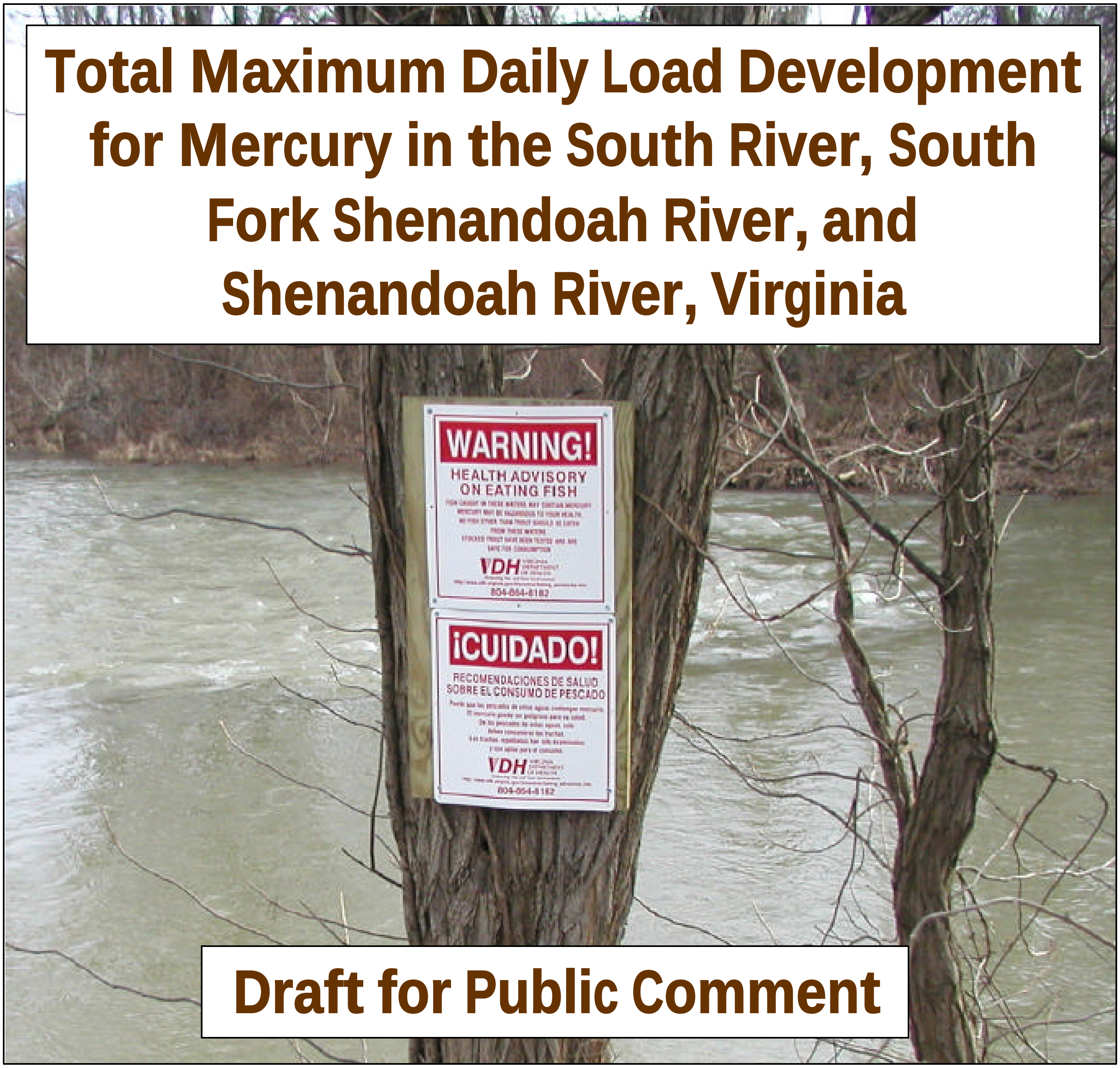
# Total Maximum Daily Load Development for Mercury in the South River, South Fork Shenandoah River, and Shenandoah River, Virginia




## Draft for Public Comment

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# Table of Contents

# List of Tables

# List of Figures

# 1. EXECUTIVE SUMMARY

*Note: This executive summary is written in a "plain language" style to be easily understood by the general public. Technical details are contained in later sections of this report and Attachment 1.*

## 1.1. BACKGROUND

In 1929, DuPont began making rayon fibers at a manufacturing plant in Waynesboro, Virginia. To help make these fibers, DuPont used a chemical that contained mercury. While DuPont recycled and reused most of the mercury, some of it went into the South River. Mercury was used at the plant from 1929 to 1950, so small losses added up to a lot of mercury over the 21 years. While it is impossible to know exactly how much mercury went into the river, a study in the 1980s roughly estimated around 100,000 pounds of mercury in the river and flood plain. At the time, the discharge of mercury was not illegal, and no one realized that mercury was potentially harmful. Today, we know that over exposure to mercury can cause brain, nerve, and kidney problems, especially in children.

Once discharged into the South River from the DuPont plant, mercury contamination was spread downstream for over 150 miles. This includes 25 miles of the South River (from the DuPont plant downstream to Port Republic, Virginia), 100 miles of the South Fork Shenandoah River (from Port Republic to Front Royal, Virginia), and 30 miles of the Shenandoah River (to nearly the West Virginia state line). Even though mercury use at the DuPont plant stopped more than 50 years ago, fish in these rivers still contain more mercury that what is considered safe to eat.

## 1.2. THE PROBLEM – TOO MUCH MERCURY IN THE FISH

To make sure that fish are safe to eat, the Virginia Department of Health (VDH) sets limits on the amount of mercury allowed in fish from Virginia's lakes and rivers. If fish have more than 0.5 parts per million (ppm) of methylmercury (the predominant form of mercury found in fish), VDH warns people against eating fish from that river or lake. The U.S. Environmental Protection Agency (USEPA) recommends an even lower level of 0.3 ppm as safe. Fish from the

South River, South Fork Shenandoah River, and Shenandoah River are above this safe level of 0.3 ppm methylmercury (Figure 1-1).

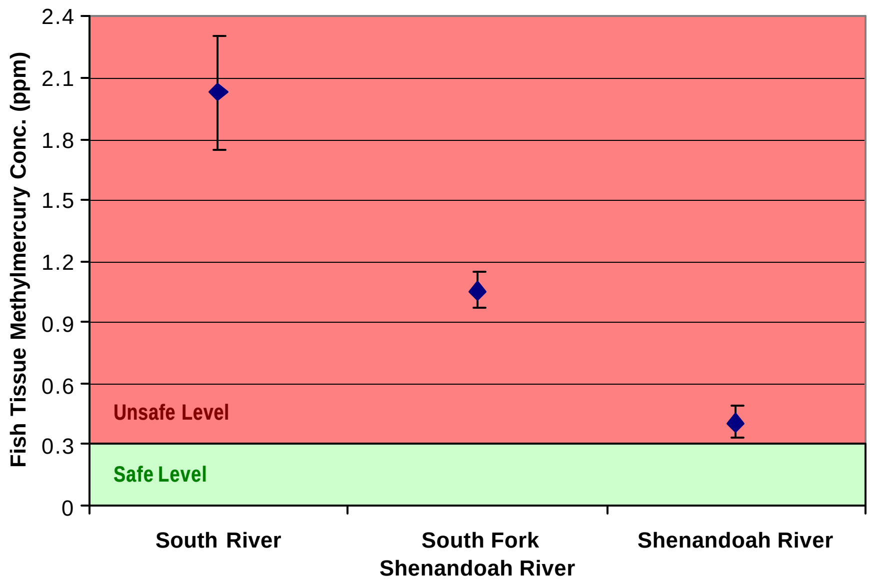


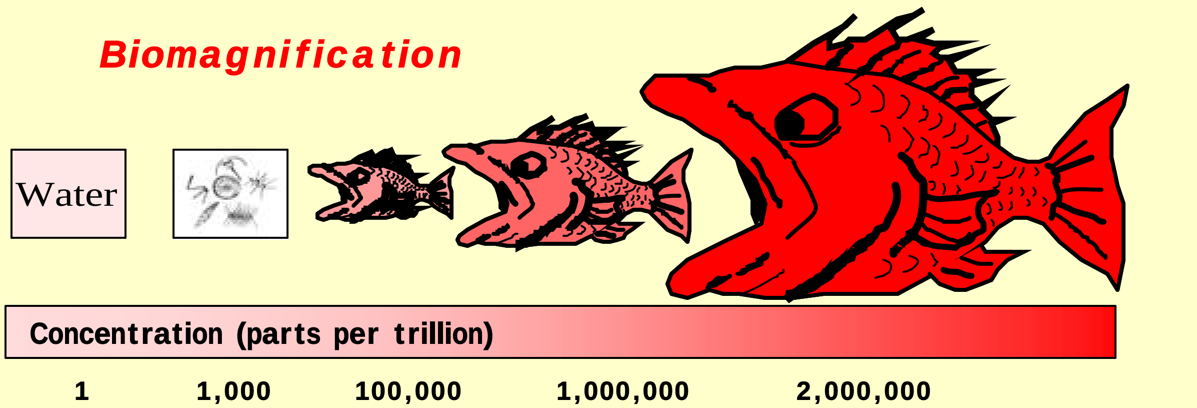

**Figure 1-1. Levels of Methylmercury in Smallmouth Bass in 2007.**

Based on the amount of methylmercury in fish from these rivers, VDH warns people not to eat fish from the South River and not to eat more than 2 meals per month of fish from the South Fork Shenandoah and mainstem Shenandoah Rivers. Pregnant women and children are warned not to eat any fish from these rivers. In addition, people should not eat carp, catfish, or suckers in the Shenandoah River and lower portions of the South Fork Shenandoah (at Front Royal, Virginia) due to another pollutant (polychlorinated biphenyls or PCBs).

Unsafe levels of methylmercury in fish have also caused these rivers to be placed on Virginia's "Dirty Waters List" (or 303(d) list). These rivers were first placed on this list in 1998. Rivers placed on the list must have clean-up plans, and this report is the first step in developing a clean-up plan for mercury in the South, South Fork Shenandoah, and Shenandoah Rivers. This report summarizes a study of mercury in these rivers and sets goals for the clean-up plan. The study is called a Total Maximum Daily Load (TMDL) Study, because it determines the maximum amount of mercury that can get into each river without producing fish that are unsafe to eat.

Why Are Fish a Problem?

Certain bacteria are able to transform mercury into methylmercury, a form of mercury that has the ability to **biomagnify** in aquatic food chains. This means that the concentration of methylmercury generally increases with each step in the food chain. For instance, algae may accumulate 1000 times more methylmercury than the water around it. When aquatic insects eat that algae they may accumulate 100 times more than what was in the algae. A small fish eating that insect may accumulate 10 times more methylmercury. A large fish that eats the smaller fish may accumulate twice as much methylmercury as the small fish. This increase at each link in the food chain means that large fish, like the ones fisherman are likely to catch and eat, may have millions of times more methylmercury than the water contains. This is why mercury contamination in a river results in advisories against eating certain fish.




## 1.3. SOURCES OF MERCURY

The original source of most of the mercury in the South River was from the DuPont plant site, but because that mercury has been spread throughout the flood plain, the current sources are much broader. A small amount of mercury also comes from natural sources or from atmospheric deposition. All of the different mercury sources identified in the study are described below:

- Point Sources – A total of 14 businesses and towns are permitted to discharge treated wastewater into the South River. This study measured the amount of mercury in all three of the industrial discharges and the two largest municipal discharges. Overall, the amount of mercury from these sources was relatively small, but the former DuPont plant contributed the most. DuPont continues to own the property and leases the manufacturing site to Invista. Even though Invista does not currently use mercury in its operations, mercury continues to be released from contaminated soil and sediment in drainage pipes on the site. Under a federal program that directs clean up of contaminated sites (the Resource Conservation and Recovery Act), DuPont is actively trying to find and clean up these sources of mercury on the plant site.

- Atmospheric Deposition – A small amount of mercury can come from atmospheric deposition, or fallout from the air. Coal naturally contains some mercury, so when it is burned, the mercury is released into the air. That mercury can then fall back to the ground some distance away. Atmospheric deposition of mercury in the South River watershed was estimated from testing at air monitoring stations along the Blue Ridge Mountains.

- Runoff – Some mercury in the soil can make its way to the South River through runoff. When rainwater moves soil from the land to the stream, mercury that is attached to that soil gets moved too. Runoff can carry mercury that is naturally occurring in the soil, mercury that has fallen onto the soil from atmospheric deposition, or mercury from the DuPont plant that has contaminated the river flood plain. The majority of mercury in runoff is from erosion of the contaminated flood plain. Floods during the period that mercury was being used by DuPont deposited mercury on the flood plain, and it is slowly making its way back to the river through erosion and runoff.

- Groundwater – Mercury that is in groundwater can add to the amount of mercury in the South River. Mercury in groundwater can come from rainwater itself or from mercury in the soil that is picked up as rainwater drains through it. This study measured the amount of mercury in groundwater near the DuPont plant site and in the contaminated flood plain further downstream.

- Interflow – Interflow is a type of groundwater that discharges quickly after a rain. Interflow can carry mercury from the atmosphere or mercury that is picked up from the soils.

- Stream Banks – Mercury can also come from the banks of the river. Like the flood plain, the river banks downstream of the DuPont plant site have much higher levels of mercury than banks upstream of the plant site. Erosion of those banks can add mercury to the river.

## 1.4. COMPUTER MODELING

The U.S. Geological Survey (USGS) used a computer model called the Hydrological Simulation Program – Fortran (or HSPF) to track mercury from its different sources, to the South River, and then downstream to the South Fork Shenandoah River. The amount of mercury that ends up in the river depends on a lot of different factors, including: the amount of mercury available from each source, the timing of inputs from those sources, how much and when it rains, how much runoff is generated, how the mercury binds with sediment in the river, and how sediment moves within the river. The model considered these and other factors to estimate the amount of mercury in the South River at any given time. To make sure that the estimates are accurate, the model was tested with real-world data. The model was used to estimate mercury levels in the South River from April 2005 to April 2007, and these estimates were compared to mercury samples collected from the river during that time period. Once the model was calibrated, or adjusted to successfully match the real-world data, it could be used to make predictions about how mercury levels in the South River might change if mercury sources were controlled.

Frequently Asked Question:

*Why use a computer model?*
Sampling and testing tells you a lot about the present and the past, but nothing about the future. A computer model is a tool that can help you make predictions about the future. This is necessary to figure out how much effort is needed to clean up a stream.

## 1.5. CURRENT CONDITIONS

The USGS used the computer model to figure out where the mercury in the South River was currently coming from. Figure 1-2 shows that the majority of the mercury in the South River (84%) comes from the banks (or channel margins). A smaller portion (15%) comes from runoff. Most of that mercury in runoff is from mercury in the contaminated flood plain that runs off with sediment. The remaining sources, which include groundwater, atmospheric deposition, and point sources, add up to only about 1% of the total amount of mercury that enters the South River.

The percentages given in Figure 1-2 represent mercury loads to the whole South River during an average year. Of course on any given day, the amount of mercury coming from each source could be very different from these percentages. For instance, the contribution from point sources and groundwater would be much greater during dry periods when there is no runoff and very little bank erosion. Throughout an average year, though, the amount of mercury coming from banks and runoff swamp all other sources of mercury.

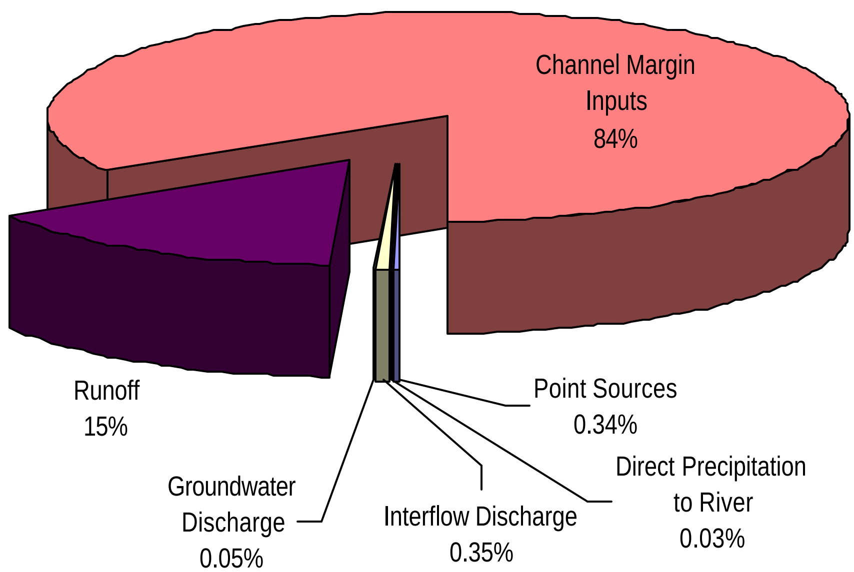
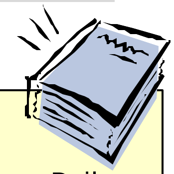



**Figure 1-2. Where is the Mercury Currently Coming From?**

## 1.6. FUTURE GOALS (THE TMDL)

After figuring out where mercury in the South River is currently coming from, the computer model was used to figure out how much mercury loads need to be reduced to clean up the South River. The ultimate goal is for people to be able to safely eat fish from the South River, South Fork Shenandoah, and Shenandoah Rivers. To do this, there will need to be an overall 99% reduction in the amount of mercury entering the South River. This goal can be achieved by reducing atmospheric and interflow inputs by 19%, reducing point source inputs by 83%, reducing runoff loads by 96%, and eliminating channel margin loads (Table 1-1). If these reductions were made, less than 2,029 grams of mercury per year would enter the South River. This safe amount, known as the total maximum daily load (TMDL), is the maximum amount of mercury that can enter the South River and still produce fish that are safe to eat. A small portion of this amount (112 g per year) is reserved for the permitted sewage and industrial treatment plants in the area (point sources), but most of the amount allows for mercury coming from the air and land surface (nonpoint sources) (Table 1-2). The good news is that if these reductions are made in the South River, no additional mercury reductions will be needed in the South Fork Shenandoah or Shenandoah Rivers. Fish in these rivers should be safe to eat if the necessary reductions are made in the South River, where the mercury problem begins.



Definition:

TMDL – Total Maximum Daily Load. This is the amount of a pollutant that a stream can receive and still meet water quality standards. The term TMDL is also used more generally to describe the state's formal process for cleaning up polluted streams.

**TMDL = WLA+LA+MOS**
where,
WLA = wasteload allocation
LA = Load allocation
MOS = Margin of safety

**Table 1-1. Reductions in Mercury Sources Needed to Clean Up the South River.**

| Source | Mercury Reductions Necessary to Produce Fish that are Safe to Eat | Mercury Load After Reductions (g/yr) | Explanation of Reductions |
|---|---|---|---|
| Precipitation directly to the river | 19% | 45 | Should be met through new air permitting rules |
| Interflow discharge | 19% | 558 | |
| Groundwater discharge | 0% | 99 | Reductions in groundwater are difficult to implement so none are called for |
| Runoff | 96% | 1,216 | A 96% reduction is the same as returning flood plain soils to background levels |
| Channel margin inputs | 100% | 0 | Elimination of virtually all of the mercury from the banks will be needed |
| Point sources | 83% | 112 | An 83% reduction means point sources discharge less than 3.8 ng/L of mercury |
| Total | 99% | 2,029 | |

The necessary mercury reductions in the South River are very large (99%) and will be difficult to achieve by simply controlling sources of mercury to the South River. Complete restoration of an edible fishery may require innovative approaches that bind or remove mercury in the river or slow the process by which mercury is brought into and moved through the food chain.

**Table 1-2. Total Maximum Daily Loads of Mercury in the South River, South Fork Shenandoah River, and Shenandoah River that Will Meet Water Quality Standards.**

| Stream | Amount from Permitted Point Sources (WLA) (g/yr) | Amount from Nonpoint Sources (LA) (g/yr) | Margin of Safety | Total Maximum Daily Load (g/yr) |
|---|---|---|---|---|
| South River | 112 | 1917 | Implicit | 2029 |
| South Fork Shenandoah River | 112 | 4008 | Implicit | 4120 |
| Shenandoah River | 112 | 5948 | Implicit | 6060 |

## 1.7. WHAT HAPPENS NEXT

The Virginia Department of Environmental Quality (VADEQ) will ask for public comment on this report and then submit it to the USEPA for approval. This report sets the clean-up goal for the South River, but the next step is a clean-up plan (or Implementation Plan) that lays out how that goal will be reached. The clean-up plan will set intermediate goals and describe actions that should be taken to clean up the South River. Some of the possible actions are listed below:

- Finding and removing mercury on the plant site
- Reducing mercury in point source discharges
- Stabilizing or restoring eroding stream banks
- Decreasing runoff of mercury contaminated soil from the flood plain
- Finding and removing (or immobilizing) hot spots of mercury contamination in sediments, banks, or the flood plain
- Discovering ways to reduce the amount of mercury that gets into the food chain

> **Interesting Fact:**
>
> The TMDL for South River is 2029 grams of mercury per year. This is about as much mercury as in 1,000 thermometers.

The clean-up plan will evaluate these and other options for reducing mercury in fish. The plan will consider the level of effort and the associated costs with each potential action and will select a set of reduction strategies that most efficiently restore the fishery. The clean-up plan will also identify potential sources of money to help in the clean-up efforts.

VADEQ will continue to sample fish in the South River, South Fork Shenandoah, and Shenandoah Rivers to monitor the progress of clean-up. This sampling will let us know when the clean-up has reached certain milestones listed in the plan. The ultimate milestone is for fish in these rivers to be safe to eat. When we reach that point, fish consumption advisories on the rivers can be removed.

# 2. INTRODUCTION

## 2.1. WATERSHED LOCATION AND DESCRIPTION

The South River is located primarily in Augusta County, Virginia (Figure 2-1). The South River is 50.8 miles in length and flows north from its headwaters in southern Augusta County, through the City of Waynesboro, and into Rockingham County. In Port Republic, Virginia, the South River joins with the North River to form the South Fork of the Shenandoah River. The drainage area of the South River is 235 square miles (607 $km^2$), with 89% in Augusta County, 6% in the City of Waynesboro, and 5% in Rockingham County.

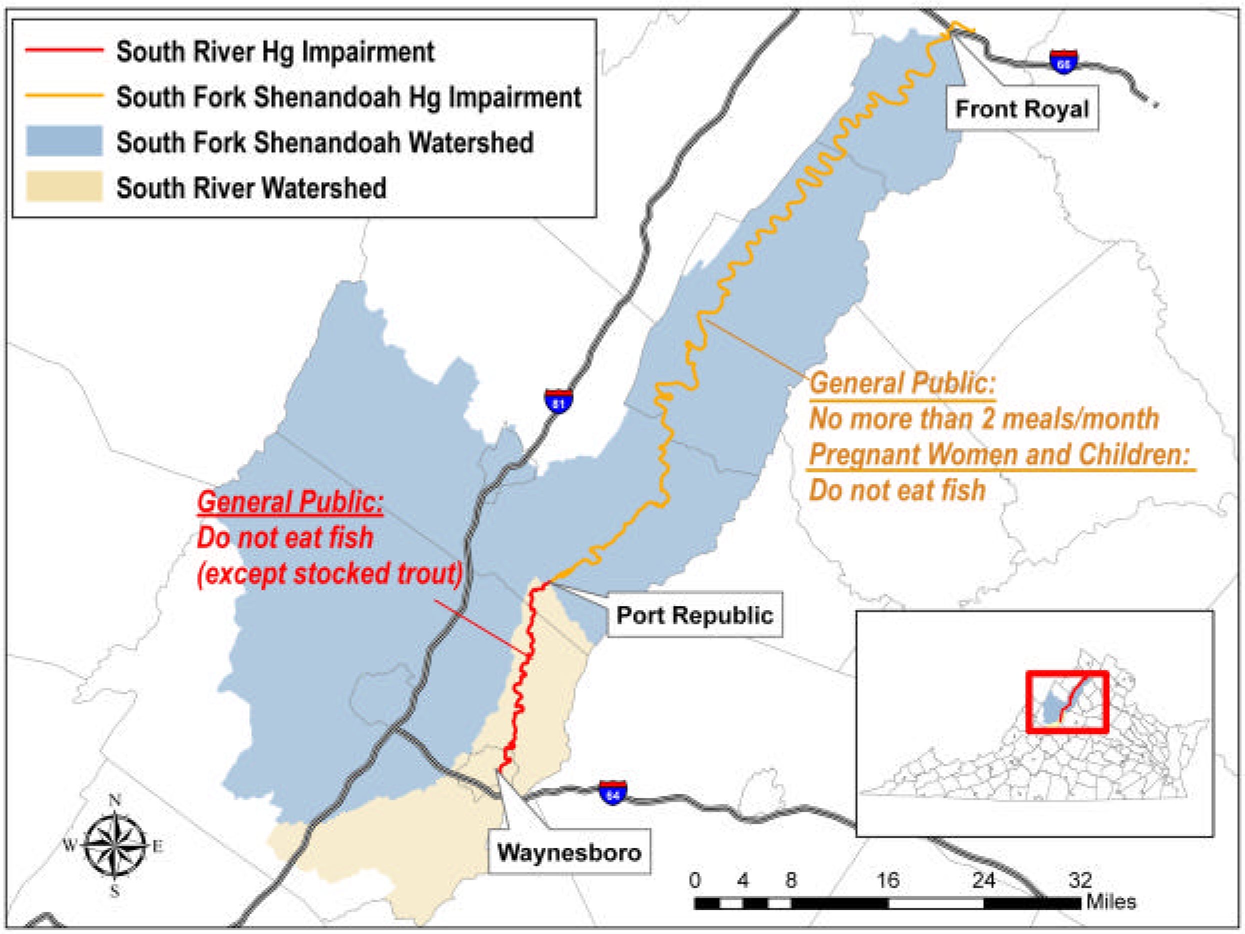



**Figure 2-1. Fish Consumption Advisories for Mercury in the South River and South Fork Shenandoah River.**

The South Fork Shenandoah River is located in Rockingham, Page, and Warren Counties, Virginia. The South Fork Shenandoah River is approximately 100 miles in length and flows north from Port Republic, Virginia, to Front Royal, Virginia, where it joins with the North Fork of the Shenandoah to form the Shenandoah River. The Shenandoah River drains to the Potomac River, which ultimately flows to the Chesapeake Bay. The South Fork Shenandoah River drains approximately 1,700 square miles (4,500 $km^2$). The South River contributes 14% of this drainage area, the North River contributes 48%, and 38% drains directly to the South Fork Shenandoah River. Land use within the South Fork Shenandoah watershed is mostly forested (58%), with 38% in agriculture and only 4% in residential and urban uses (VADCR, 2008).

## 2.2. BACKGROUND

Since 1977, the South River and South Fork Shenandoah River have been posted with fish consumption advisories due to mercury contamination. Currently, VDH advises no consumption of wild fish from the South River downstream of the DuPont footbridge in Waynesboro and no more than two meals per month for fish from the South Fork Shenandoah River (Figure 2-1). Pregnant women and children are advised to eat no wild fish from the South River or South Fork Shenandoah River. Due to fish movement, small sections of the North Fork Shenandoah River and mainstem Shenandoah River are listed with the same advisory as the South Fork Shenandoah River. This applies to the North Fork Shenandoah River from the confluence with the South Fork upstream to the Riverton Dam and the mainstem Shenandoah River from the confluence with the South Fork downstream to the Warren Power Dam.

Mercury contamination in the South River originally resulted from historic releases from a DuPont manufacturing facility in Waynesboro, Virginia. Between 1929 and 1950, DuPont used a mercuric sulfate catalyst in the manufacturing of acetate fibers. While the majority of the mercury catalyst was captured and reused, losses from the facility to the river over the 21 years of use resulted in widespread mercury contamination downstream (SWCB, 1980). A 1989 study provided a rough estimate of 1,800 pounds of mercury in downstream river sediments and 97,200 pounds of mercury in flood plain soils (Lawler, Matusky & Skelly Engineers, 1989). While initial studies indicated that fish mercury concentrations would slowly decrease without any remedial action (Lawler, Matusky & Skelly Engineers, 1982), no discernable declines in fish tissue levels have been observed in the 30 years since mercury contamination in the river was first discovered.

Results from the most recent fish sampling in 2007 showed that the current fish consumption advisories are warranted. Above the DuPont footbridge in Waynesboro, methylmercury in fish fillets averaged <0.3 ppm for all fish species. At monitoring sites below the DuPont footbridge, methylmercury levels in smallmouth bass averaged from 0.644 to 3.107 ppm, white suckers averaged from 0.36 to 2.366 ppm, and redbreast sunfish averaged from 1.038 to 2.147 ppm (VADEQ, 2008a). Stocked rainbow trout were all well below 0.3 ppm. Along the length of the South Fork Shenandoah, methylmercury levels in smallmouth bass averaged from 0.733 to 1.326 ppm, white suckers averaged 0.383 to 0.781 ppm, redbreast sunfish averaged 0.456 to 0.644 ppm, channel catfish averaged 0.761 to 0.878 ppm, and northern hogsuckers averaged 0.305 to 0.483 ppm.

In 1998, USEPA issued a Resource Conservation and Recovery Act (RCRA) permit to DuPont for investigation and clean up of residual mercury contamination on the plant site. DuPont is currently in the process of conducting a RCRA facility investigation at the site. This activity has involved groundwater, stormwater, and soil testing on the plant site. After completing the investigation, corrective actions will be taken to address solid waste management units that pose a human health or ecological risk. In addition, DuPont has been investigating mercury contamination in the South River ecosystem as part of a settlement agreement with the Natural Resources Defense Council and the Sierra Club. This six-year study includes a first phase that characterizes mercury impacts in the South River ecosystem and a second phase that focuses on specific sources of mercury and mercury methylation sites. Results from these and other South River studies are periodically presented to the South River Science Team, a collection of state and federal agencies, stakeholders, and researchers interested in South River mercury issues.

In 2004, DuPont sold the manufacturing assets of the Waynesboro plant to Koch Industries, Inc., and the name of the facility was changed to Invista. DuPont continues to own the property and retains responsibility for environmental clean up under the RCRA permit. Invista now owns and operates the manufacturing assets, including the stormwater and wastewater outfalls permitted by VADEQ.

## 2.3. IMPAIRMENT LISTING

Based on the continuing fish consumption advisory on the South River and South Fork Shenandoah River, VADEQ placed these rivers on the 1998 303(d) Impaired Waters List (VADEQ, 1998). The 1998 listing included only 103.4 miles of river, including the South River downstream from the DuPont footbridge and the South Fork Shenandoah River downstream to the Page/Warren County line. Since that original listing, the impairment listing has expanded based on additional monitoring, consideration of fish movement, and changes in the fish tissue methylmercury criterion.

The current fish consumption impairment listing for mercury includes 156.09 miles of river (VADEQ, 2008b). This includes the South River from the Invista (formerly DuPont) discharge to the confluence with the North River, the full length of the South Fork Shenandoah River, a short section of the North Fork Shenandoah River upstream to the Riverton Dam, and the mainstem Shenandoah River to its confluence with Craig Run (Table 2-1). The current impairment listing includes an additional 26 miles on the mainstem Shenandoah River, which extends further downstream than the existing fish consumption advisory. This segment was added to the impaired length in the 2008 assessment due to additional fish tissue monitoring further downstream. The fish consumption advisory has not been lengthened to include this portion for mercury, because this segment already contains a more restrictive fish consumption advisory for PCBs (do not eat carp, channel catfish, and sucker species; no more than 2 meals/month for bass and sunfish species).

**Table 2-1. Fish Consumption Impairment Listing for Mercury.**

| River | Upstream Extent | Downstream Extent | Stream Miles |
|---|---|---|---|
| South River | Invista Discharge | Confluence with North River | 24.63 |
| South Fork Shenandoah River | Confluence of South River and North River | Confluence with NF Shenandoah | 100.96 |
| North Fork Shenandoah River | Riverton Dam | Confluence with SF Shenandoah | 0.67 |
| Shenandoah River | Confluence of North Fork and South Fork Shenandoah | Confluence with Craig Run | 29.83 |
| | | **Total** | **156.09** |

## 2.4. DESIGNATED USES AND APPLICABLE WATER QUALITY STANDARDS

Virginia's Water Quality Standards (9 VAC 25-260) consist of designated uses established for water bodies in the Commonwealth, and water quality criteria set to protect those uses. Virginia's Water Quality Standards protect the public and environmental health of the Commonwealth and serve the purposes of the State Water Control Law (§62.1-44.2 *et seq.* of the Code of Virginia) and the federal Clean Water Act (33 USC §1251 *et seq.*).

### 2.4.1. Designation of Uses (9 VAC 25-260-10)

Virginia's Water Quality Standards (9 VAC 25-260) establish the following designated uses:

> *"A. All state waters, including wetlands, are designated for the following uses: recreational uses, e.g., swimming and boating; the propagation and growth of a balanced, indigenous population of aquatic life, including game fish, which might reasonably be expected to inhabit them; wildlife; and the production of edible and marketable natural resources, e.g., fish and shellfish"* (SWCB, 2006).

The above listed uses are designated for all state waters, including the South River, South Fork Shenandoah, and Shenandoah Rivers. These rivers do not support the fish consumption designated use (i.e., production of edible and marketable natural resources) due to the mercury contamination and resulting fish consumption advisories.

### 2.4.2. Applicable Water Quality Criterion for Mercury

Virginia's current mercury criterion for the protection of human health from fish consumption is a water column total mercury concentration of 0.051 ug/L (9 VAC 25-260-140). This criterion was developed based on the methodology provided in the 1980 *Ambient Water Quality Criteria for Mercury* (USEPA, 1980). Using this methodology, Virginia calculated the criterion according to the following equation and values.

$$WQC = \frac{RfD \times BW}{FI \times PBCF} \qquad [2\text{-}1]$$

Where,

$WQC$ = Water Quality Criterion (0.051 ug/L),

$RfD$ = Reference Dose (0.1 ug/kg/d),

*BW* = Body Weight (70 kg),

*FI* = Fish Ingestion Rate (0.0187 kg/d), and

*PBCF* = Practical Bioconcentration Factor (7342.6 L/kg).

While this methodology and these assumed values were appropriate at the time, advancements in the scientific understanding of methylmercury bioaccumulation and health effects have led to new methodologies and assumptions for developing more protective water quality criteria for mercury. In response, USEPA published the *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* in 2000 (USEPA, 2000) and *Water Quality Criterion for the Protection of Human Health: Methylmercury* in 2001 (USEPA, 2001). In the 2001 Methylmercury Criterion Document, USEPA established a new fish tissue residue criterion of 0.3 ppm methylmercury in fish tissue using the following equation and assumptions:

$$TRC = \frac{BW \times (RfD - RSC)}{FI} \qquad [2\text{-}2]$$

Where,

*TRC* = Fish tissue residue criterion (0.3 ppm methylmercury in fish tissue),

*BW* = Human body weight (70 kg),

*RfD* = Reference dose (0.0001 mg/kg),

*RSC* = Relative source contribution ($2.7 \times 10^{-5}$ mg/kg), and

*FI* = Fish intake rate (0.0175 kg/d).

This fish tissue residue criterion replaces the ambient water quality criterion for total mercury published in 1980. This new criterion also represents a significant change in methodology by being expressed in terms of a fish tissue residue rather than a water column concentration. USEPA's *Draft Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion* (USEPA, 2006) explains that, among other reasons, this approach is preferred because it avoids the need for assuming standard bioaccumulation factors (BAFs), which are highly site-specific. When TMDLs or NPDES (National Pollutant Discharge Elimination System) permits necessitate the establishment of a water concentration-based criterion, USEPA recommends using a site-specific bioaccumulation factor or bioaccumulation model to translate the 0.3 ppm fish tissue criterion.

In response to USEPA's updated water quality criterion for mercury, the Commonwealth of Virginia has proposed to revise the State Water Quality Standards to adopt the new 0.3 ppm criterion for methylmercury (SWCB, 2008). This revision to the Water Quality Standards was proposed on March 31, 2008, and public comment was accepted from March 31 to May 30, 2008. Final adoption of the new methylmercury criterion is expected in 2009.

Based on USEPA's recommended water quality criterion for methylmercury and Virginia's proposed water quality standards revision, **the applicable water quality criterion for this TMDL was determined to be a fish tissue methylmercury concentration of 0.3 ppm**. This criterion was then translated to a protective water quality target using a site-specific empirical bioaccumulation model.

It should be noted that background methylmercury concentrations in fish that are upstream from the mercury contaminated area are just below this threshold. Methylmercury concentrations in size-normalized smallmouth bass at the upstream reference site average 0.29 ppm. This indicates that restoration of the fish consumption designated use will require reductions in mercury loadings to near background levels.

### 2.4.3. Development of a Site-specific Water Quality Target

In order to develop a TMDL that links mercury loadings to the applicable fish tissue criterion, it is necessary to translate the fish tissue criterion to a protective water quality target concentration. USEPA recommends several appropriate approaches that can be used to make this translation (USEPA, 2001). These approaches include using a mechanistic bioaccumulation model, an empirical bioaccumulation model, or a bioaccumulation factor. Each of these approaches has distinct advantages, disadvantages, and data requirements. Based on the data available for the South River, a site-specific empirical bioaccumulation model approach was used to translate the 0.3 ppm methylmercury fish tissue criterion to a protective water quality target concentration. The remainder of this section describes the rationale for selecting this approach and the details of developing the translator.

Mechanistic bioaccumulation models were initially considered for translating the fish tissue criterion. Mechanistic models are attractive because they directly represent many factors that may be important in mercury methylation and bioaccumulation. However, a limited number of such mechanistic models have been developed, and those that have been developed have not been applied to free-flowing rivers. In addition, the information necessary to properly parameterize a mechanistic model is not currently available for the South River. In consultation with the South River Science Team (SRST), it was determined that the present understanding of specific factors controlling mercury methylation and bioaccumulation in the South River was not sufficient to adequately support the development of a mechanistic bioaccumulation model.

The bioaccumulation factor approach was also considered for translating the fish tissue criterion in the South River. A bioaccumulation factor (BAF) is the ratio of mercury in fish tissue at the site to mercury in the water column. Using this approach, the fish tissue criterion can simply be divided by the BAF to obtain a protective water quality target concentration. The BAF approach has the advantage of considering site-specific bioaccumulation information without having to define and individually model those biotic and abiotic factors controlling bioaccumulation. The approach allows for more simplified modeling of total mercury loads. One of the disadvantages of the BAF approach is that it assumes a linear relationship between mercury in fish tissue and mercury concentrations in the water column, such that BAFs are independent of water column concentrations. Southworth *et al.* (2004) suggest that this assumption is unlikely, particularly at highly contaminated sites, such as the South River. Using data from 13 freshwater streams in Tennessee, Kentucky, North Carolina, and Virginia (including the South River and South Fork Shenandoah River), Southworth *et al.* demonstrated that BAFs were lower at contaminated sites than uncontaminated sites and tended to be lowest in the most contaminated systems. If BAFs indeed decrease with increasing mercury contamination levels, TMDLs based on BAFs calculated at contaminated sites will under predict the level of reductions needed to protect fish consumption uses. As reductions in total mercury loadings are made, BAFs will increase, and resulting reductions in fish contaminant levels will be less than anticipated.

To avoid this under prediction in the South River TMDL project, VADEQ decided to use a site-specific empirical bioaccumulation model that considers the non-linear relationship between mercury in fish tissue and mercury in the water column. The South River and South Fork Shenandoah River system contains approximately 130 miles of river that generally decreases in mercury contamination moving downstream away from the historical point source of mercury in

Waynesboro. VADEQ collected water column and fish tissue mercury levels at numerous sites along the stretch of these rivers, and indeed BAFs decrease with increasing levels of mercury contamination. With collocated water column and fish tissue mercury levels that span the range of contamination, an empirical model of the non-linear water column to fish tissue mercury relationship could be developed and used to predict a water column target concentration that would be protective of the 0.3 ppm fish tissue criterion. The remainder of this section discusses the development of this site-specific empirical bioaccumulation model.

#### 2.4.3.1. Data Collection

VADEQ collected water column and fish tissue mercury samples from ten stations along the South River and South Fork Shenandoah River (Figure 2-2). Fish and water column samples were either collected from the same location or in close proximity depending on river access for fish sampling gear and available fish habitat. At seven of these stations, VADEQ has conducted bimonthly water column sampling of mercury since 2002. The remaining three stations (1BSTH014.49, 1BSTH004.21, and 1BSSF100.10) were added to the bimonthly sampling schedule in 2004. Water column samples were collected by submerging a 4L plastic bottle to 1/3 of the stream depth in the mid channel. Ultra clean sampling techniques involving "clean hands/dirty hands" procedures were used according to VADEQ standard operating procedures for collection of trace elements (VADEQ, 2005). An aliquot of the collected sample was filtered in the field through a 0.45 µm filter for analysis of filter-passing mercury (procedurally defined as "dissolved" mercury). This sample and an unfiltered aliquot for total mercury analysis were packed on ice and shipped to the Division of Consolidated Laboratory Services for analysis. Total and filter-passing mercury were analyzed using USEPA Method 1631 (USEPA, 2002).

Fish data collected from 1999 through 2005 were used in the development of a site-specific water quality target. Fish were collected during the spring through fall with the use of backpack electroshocking equipment in wadeable stream sections or boat mounted electroshocking equipment in deeper stream segments. The sampling targeted smallmouth bass as representative predators, redbreast sunfish as representative grazers, and white suckers as representative bottom feeders. If the target organisms were not present at a specific sampling location, other available species within the predator, grazer, and bottom feeder functional groups were sampled. Up to nine fish per species within the edible size range were collected from each sampling location.

Fish were weighed and measured in the field and packed on ice for transport to VADEQ. Samples were then frozen and shipped to the Division of Consolidated Laboratory Services for analysis. Skin-on fillets from each fish were analyzed for total mercury using USEPA Method 1631 (USEPA, 2002). Results from previous studies have shown that approximately 90% of total mercury in South River fish is in the form of methylmercury (VADEQ, 2008a), so measured total mercury concentrations were multiplied by 0.9 to obtain estimated methylmercury concentrations in fish tissue.

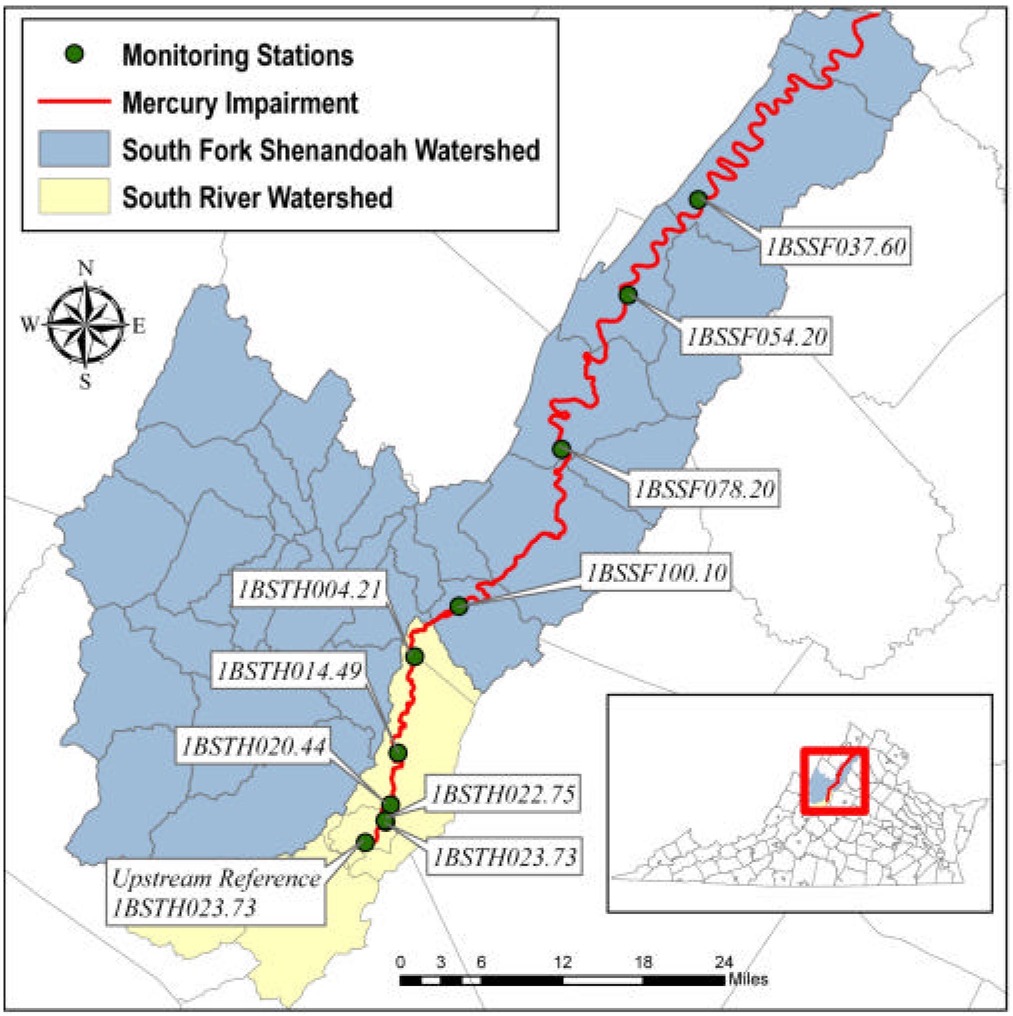



**Figure 2-2. Collocated (or Proximally Located) Water Quality and Fish Tissue Sampling Stations.**

### 2.4.3.2. Fish Tissue and Water Column Results

All fish species collected in the South River and South Fork Shenandoah River averaged above the applicable water quality criterion (0.3 ppm) with the exception of rainbow trout, which are hatchery raised and seasonally stocked in the South River (Figure 2-3). Being closer to the original source of mercury contamination, fish in the South River accumulated significantly more methylmercury than fish in the South Fork Shenandoah. In both rivers, the highest levels of methylmercury are accumulated in the piscivorus predators (largemouth bass and smallmouth bass), which fill the top trophic level in these river systems. To provide conservative estimates in the TMDL, methylmercury accumulation in these top trophic level predators were used to develop the protective water quality target concentration. Specifically, smallmouth bass were used as the target species, because smallmouth bass had the highest methylmercury levels (averaging 2.0 ppm), and these fish are the most often sought after species by anglers on these rivers.

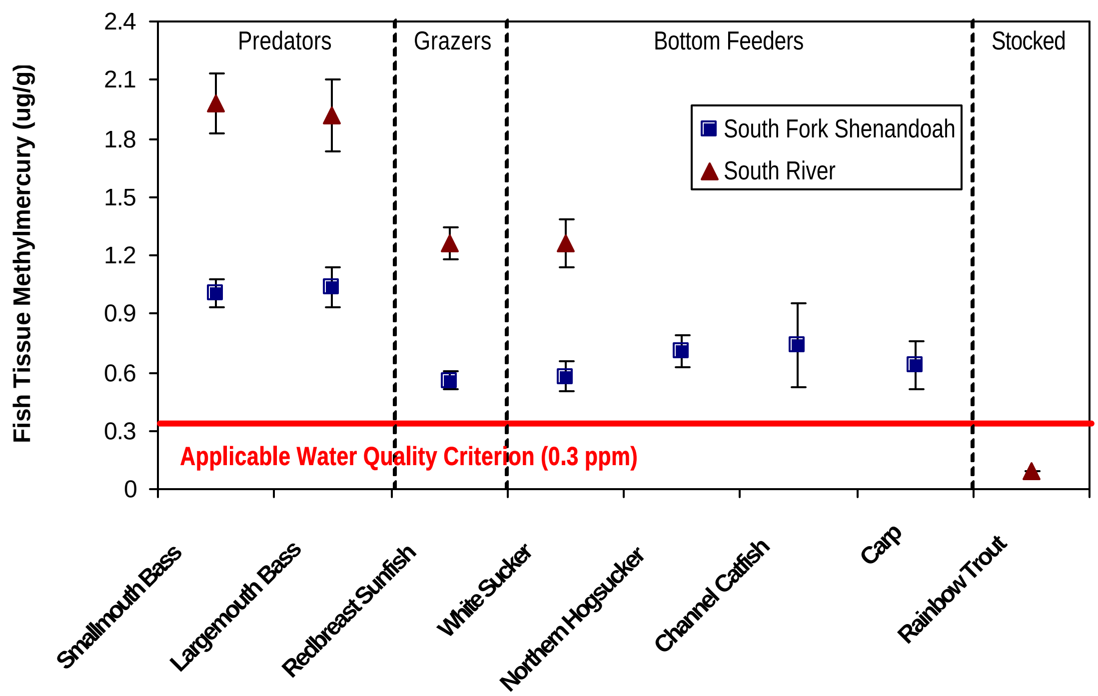



**Figure 2-3. Average Methylmercury Concentration in Fish Tissue from Various Species in the South River and South Fork Shenandoah River.**

In addition to varying by species, fish tissue methylmercury levels varied by fish size. Older, larger fish had higher body burdens of methylmercury than younger smaller fish (Figure 2-4). For this reason, fish methylmercury levels were normalized to a standard fish size in developing the protective water quality target concentration. This normalization was conducted by dividing the fish tissue methylmercury concentration of each fish by the weight of that fish, and then multiplying by a representative fish size. Separate water quality targets were developed for the South River, South Fork Shenandoah River, and Shenandoah River based on different representative fish sizes, since fish size increased with downstream increases in flow and available habitat. In each river, the size of smallmouth bass was lognormally distributed, so the representative size in each river was determined from the lognormal cumulative distribution function (Figure 2-5 through Figure 2-7). Based on the mean and standard deviation of natural log transformed data, the lognormal cumulative distribution function was used to identify the fish size in each river that would have a cumulative probability of 50%. This representative size fish was determined to be 218 g in the South River, 253 g in the South Fork Shenandoah River, and 321 g in the Shenandoah River.

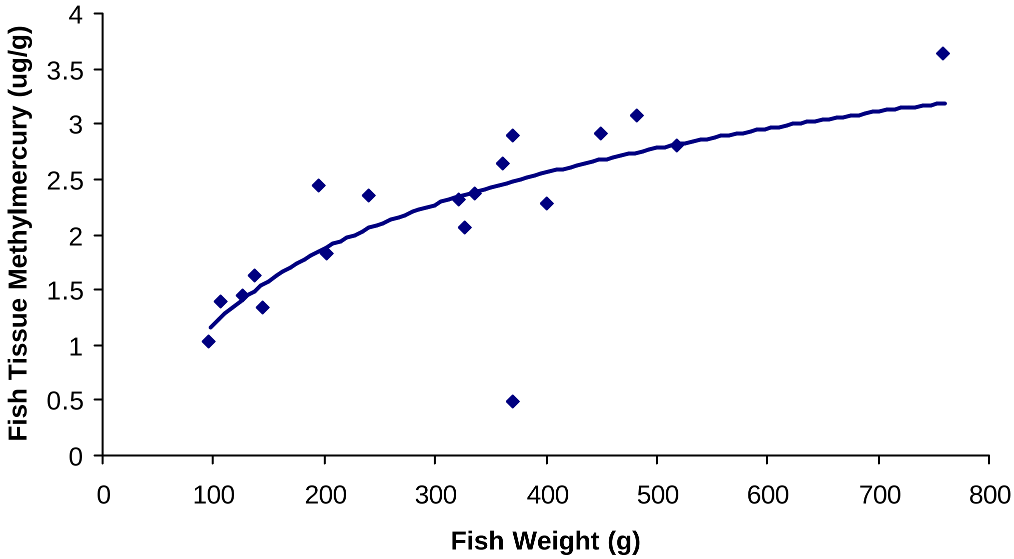



**Figure 2-4. Influence of Fish Size on Methylmercury Accumulation; Smallmouth Bass from Station 1BSTH004.21.**

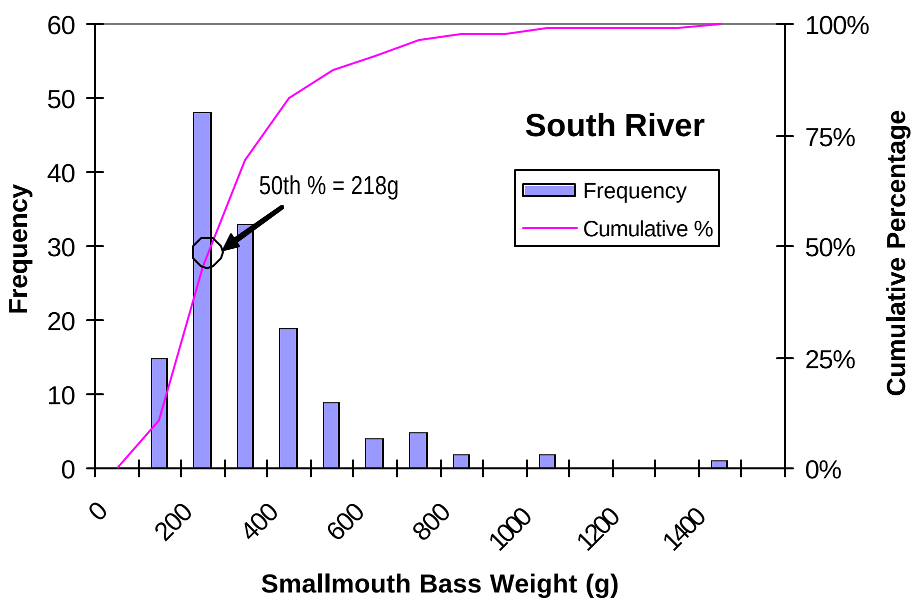



**Figure 2-5. Histogram of Smallmouth Bass Size (g) in the South River.**

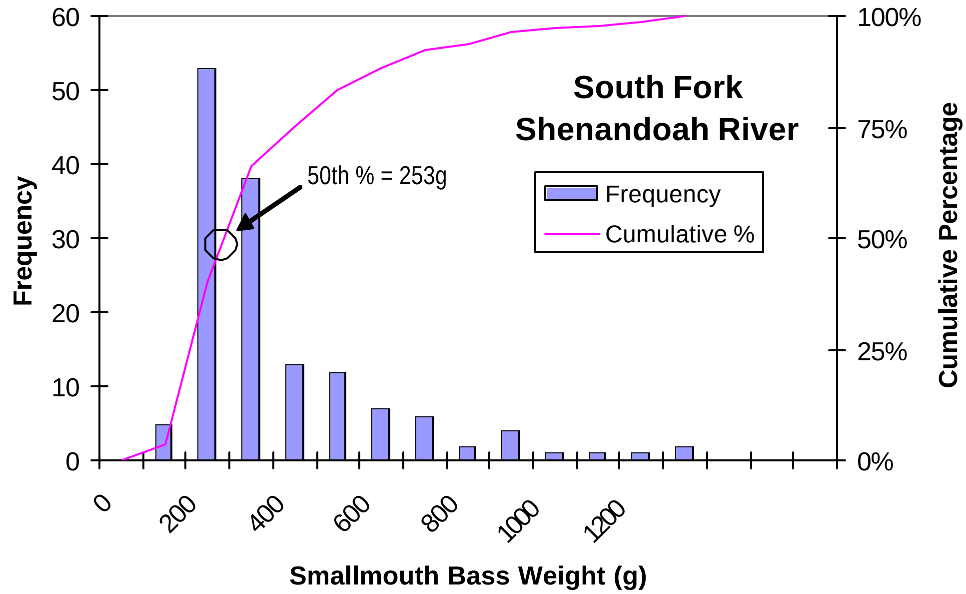



Figure 2-6. Histogram of Smallmouth Bass Size (g) in the South Fork Shenandoah River.

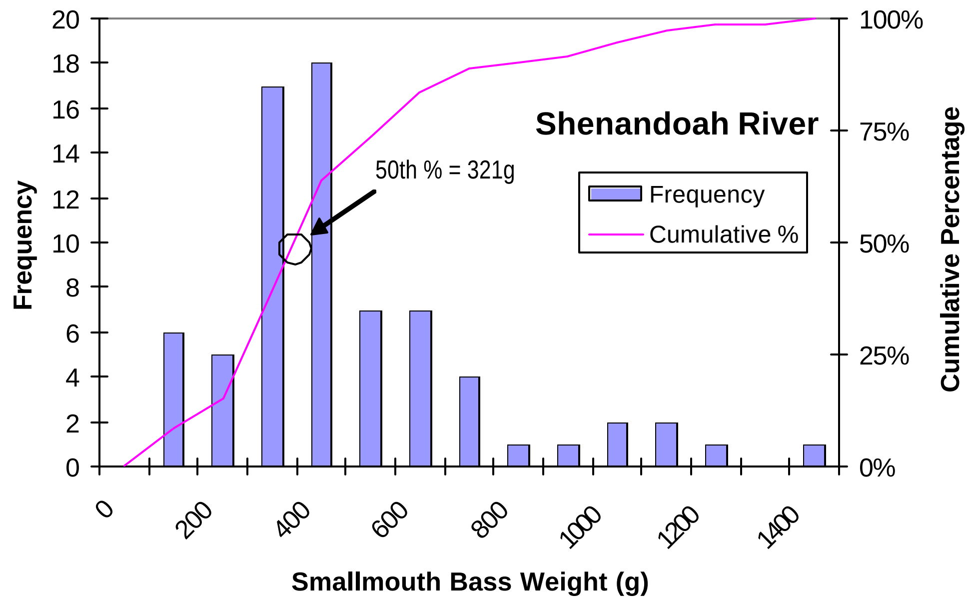



Figure 2-7. Histogram of Smallmouth Bass Size (g) in the Shenandoah River.

Normalized fish methylmercury concentrations also varied by distance downstream from DuPont (Table 2-2). This difference was due to the varying levels of mercury contamination in the system, and tracked well with total mercury concentrations in the water column (Figure 2-8). Mercury concentrations in the water column and in fish tissue increase sharply for approximately the first 10 miles downstream of DuPont (to the town of Crimora, VA). Mercury concentrations then decrease throughout the remaining length of the South River. At approximately 25 miles downstream, the South River joins with the North River to form the South Fork Shenandoah River in Port Republic, VA. Mercury concentrations decrease sharply at this point due to dilution from the additional North River flow and clean sediment load. Throughout the South Fork Shenandoah River, mercury concentrations remain relatively constant.

**Table 2-2. Mercury in Size-normalized Smallmouth Bass and Water Column in the South River and South Fork Shenandoah River.**

| Station | Distance Downstream (miles) | Normalized Fish Tissue Methylmercury[1] (ug/g) | Water Column Total Hg[1] (ng/L) |
|---|---|---|---|
| 1BSTH026.12 (reference) | -1.02 | **0.29** ± 0.19 (38) | **1.75** ± 0.62 (33) |
| 1BSTH023.73 | 1.37 | **0.90** ± 0.55 (18) | **13.1** ± 7.4 (18) |
| 1BSTH022.75 | 2.35 | **1.92** ± 1.08 (16) | **35.5** ± 25.8 (32) |
| 1BSTH020.44 | 4.66 | **2.16** ± 0.83 (19) | **83.1** ± 53.3 (32) |
| 1BSTH014.49 | 10.61 | **2.69** ± 1.35 (28) | **84.3** ± 63.5 (14) |
| 1BSTH004.21 | 20.89 | **1.76** ± 0.65 (19) | **59.1** ± 38.1 (16) |
| 1BSSF100.10 | 27.76 | **0.95** ± 0.32 (70) | **14.6** ± 12.0 (16) |
| 1BSSF078.20 | 49.62 | **0.71** ± 0.62 (28) | **11.9** ± 12.2 (31) |
| 1BSSF054.20 | 73.66 | **1.01** ± 0.39 (28) | **16.3** ± 25.3 (16) |
| 1BSSF037.60 | 90.26 | **0.78** ± 0.43 (19) | **11.0** ± 19.2 (31) |
| All sites (excluding reference) | NA | **1.33** ± 0.96 (245) | **35.7** ± 43.2 (206) |

[1] Mercury values represent mean ± standard deviation, with number of samples in parentheses. Fish tissue values were normalized to a 218 g fish, the 50% probability size fish in the South River.

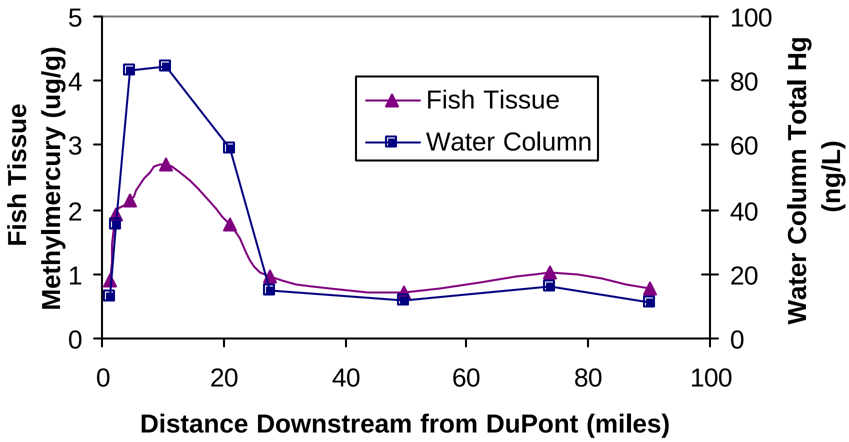



**Figure 2-8. Size-normalized Fish Tissue Methylmercury and Water Column Mercury in the South River and South Fork Shenandoah River Downstream from DuPont in Waynesboro, VA.**

#### *2.4.3.3. Empirical Bioaccumulation Model Development*

As previously discussed, site-specific information on the factors controlling mercury methylation and bioaccumulation did not allow the development of a mechanistic bioaccumulation model for the South River. However, fish tissue and water column mercury data collected by VADEQ in the South River and South Fork Shenandoah River provided a robust dataset for developing an empirical model. The developed model represents the empirical relationship between total mercury in the water column and methylmercury in fish tissue of smallmouth bass, the top trophic level consumer in the South River aquatic ecosystem. Figure 2-9 depicts the key processes of methylation, biological uptake, and trophic transfer that lead to the bioaccumulation of methylmercury in upper trophic level fish. Because the factors controlling each of these steps are not completely understood in the South River system, the empirical model directly relates the input and the ultimate outcome from this series of steps. This is not to say that the intervening steps and processes are unimportant. Rather, the empirical model inherently incorporates these processes under the prevailing environmental conditions present in the South River and South Fork Shenandoah River.

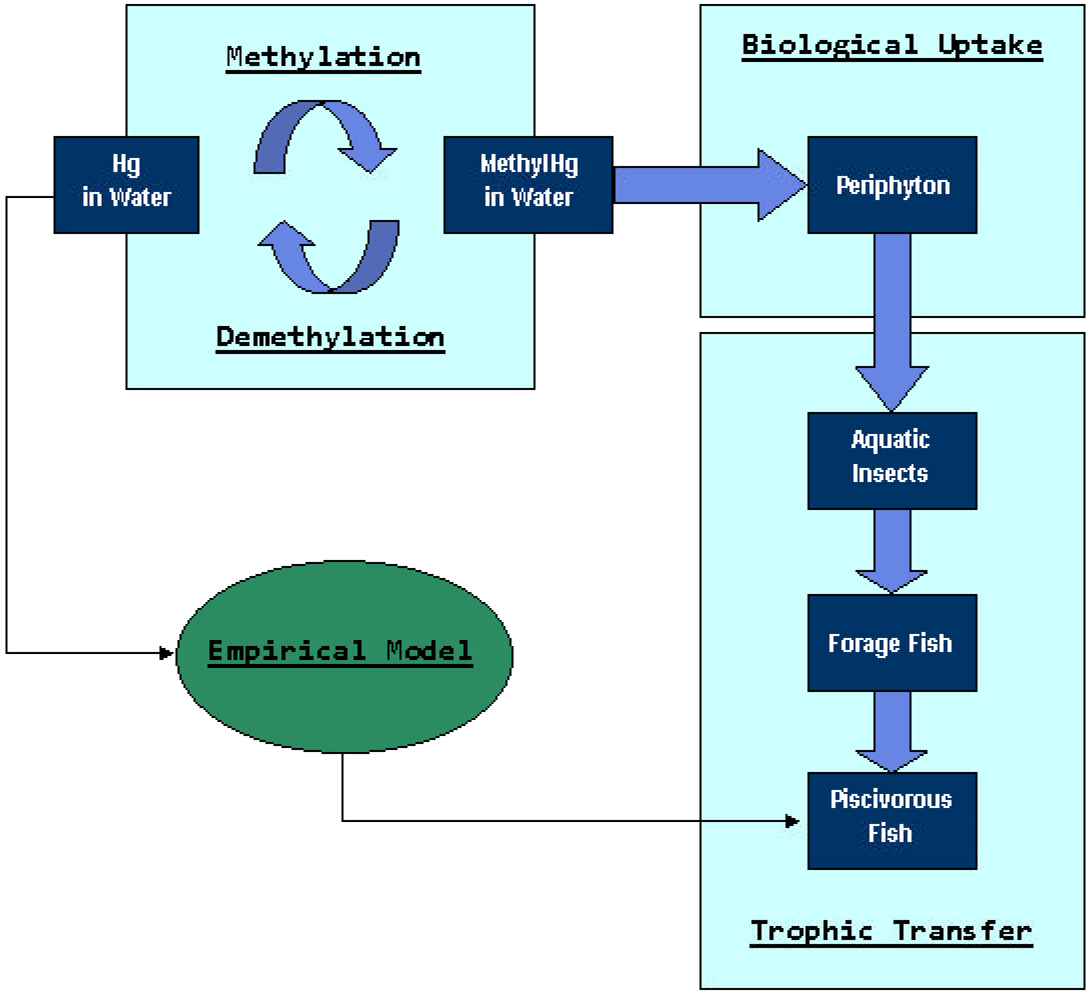



**Figure 2-9. Simplified Conceptual Model of Mercury Bioaccumulation and an Empirical Bioaccumulation Model.**

The empirical bioaccumulation model was developed from collocated fish tissue and water column mercury data collected at sites that varied in mercury contamination. This allowed the analysis of the water column mercury to fish tissue relationship across a range of mercury contamination levels. Figure 2-10 shows this relationship across nine sites in the South River and South Fork Shenandoah River. The relationship appeared to be non-linear, with the rate of increase in fish tissue methylmercury levels slowing as total mercury in the water column increased. This finding is consistent with the findings of Southworth *et al.* (2004), who demonstrated that ratios of mercury in fish tissue to total mercury in the water column (i.e., total mercury bioaccumulation factors) decreased with increasing mercury contamination levels.

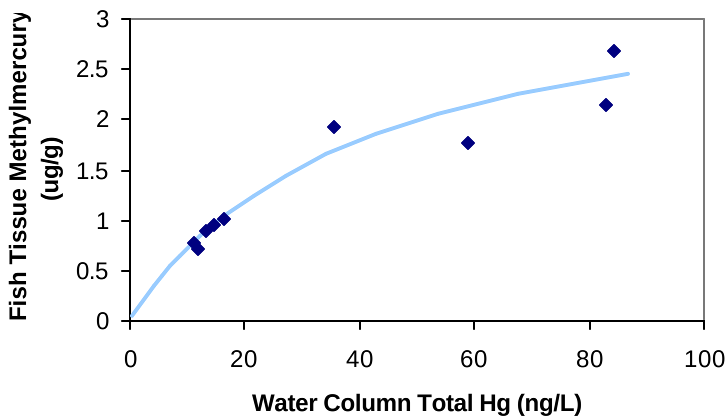



**Figure 2-10. Relationship Between Size-normalized Fish Tissue Methylmercury Levels and Total Mercury in the Water Column of the South River and South Fork Shenandoah River.**

Southworth *et al.* (2004) also hypothesized that the percent methylmercury to mercury relationship in water, and thus the related fish tissue to water column mercury relationship, would fit the form of the Michaelis-Menten equation (Figure 2-11). The Michaelis-Menten equation is a standard relationship used in biochemistry to describe the reaction rate of enzyme catalyzed reactions (Darnell *et al.*, 1990). The relationship between fish tissue methylmercury and water column mercury in the South River/South Fork Shenandoah River system (Figure 2-10) appears to fit the shape of this standard Michaelis-Menten curve (Figure 2-11). In addition to the empirical fit of the data, the underlying mechanisms involved in bioaccumulation support the fit of the data to this form. The primary step from water column mercury to bioaccumulation in fish is the methylation of inorganic mercury (Sorensen *et al.*, 1990). This step is most often carried out by sulfate-reducing bacteria (Winfrey and Rudd, 1990), and would likely be an enzyme-mediated reaction that is dependent upon the concentration of the reaction substrate (in this case, inorganic mercury). For these reasons, the Michaelis-Menten equation was used as the basis of the empirical model describing the water column mercury to fish tissue methylmercury relationship.

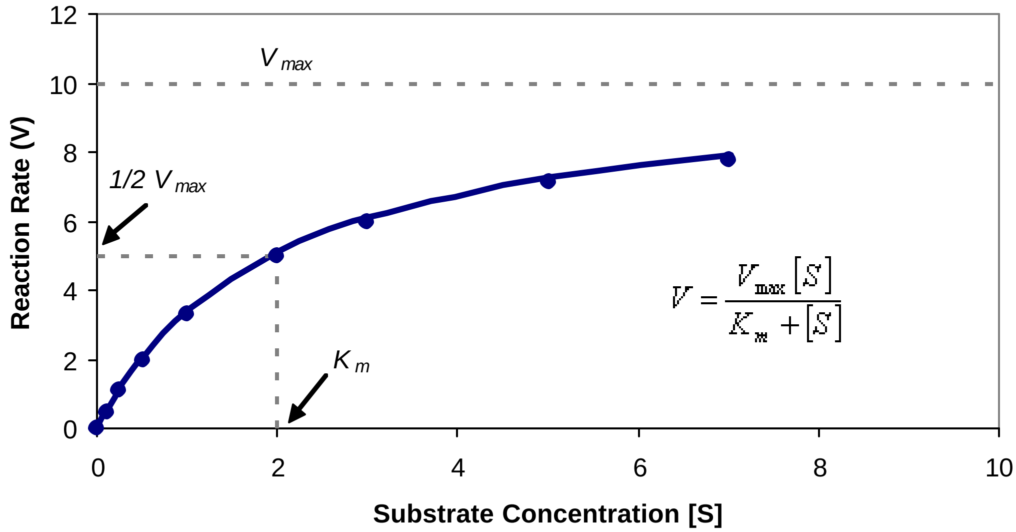



**Figure 2-11. Standard Michaelis-Menten Equation for Enzyme-mediated Reactions.**

The traditional approach to linearization of the Michaelis-Menten equation is an inverse plot, or Lineweaver-Burk plot (Lineweaver and Burk, 1934). This approach plots the inverse of the reaction rate (or in our case, the fish tissue concentration) on the y-axis and the inverse of the substrate concentration (or in our case, the water column concentration) on the x-axis. Using this approach, the water column mercury to fish tissue methylmercury relationship was linearized (Figure 2-12). The South River/South Fork Shenandoah River data fit the linearized Michaelis-Menten equation extremely well, with an $R^2$ of 0.9562. The resulting equation to describe the water column mercury to fish tissue methylmercury relationship was:

$$Hg_{Water} = \frac{a}{\left(\frac{1}{Hg_{Fish}}\right) - b} \qquad [2\text{-}3]$$

Where,

> $Hg_{Water}$ = Total mercury concentration in the water column (ng/L),
>
> $Hg_{Fish}$ = Methylmercury concentration in size-normalized smallmouth bass from South River/South Fork Shenandoah River (ug/g),
>
> $a$ = Slope of the Lineweaver-Burk plot, and
>
> $b$ = Intercept of the Lineweaver-Burk plot.

The above equation was used as an empirical bioaccumulation model to predict target water column concentrations of total mercury that would be protective of the 0.3 ppm methylmercury fish tissue criterion. This equation was evaluated independently for the South River, South Fork Shenandoah River, and mainstem Shenandoah River. Fish sizes generally increase as the size of the rivers increases downstream, so the human health risk of eating larger contaminated fish would also increase. This was reflected in developing separate target water column concentrations for each river based on the respective fish sizes in the different rivers (see Section 2.4.3.2). Table 2-3 shows the resulting target water column concentrations of total mercury in each river. In the South River, the target water column concentration was calculated to be 3.8 ng/L total mercury. The target concentration was 3.2 ng/L in the South Fork Shenandoah River and 2.5 ng/L in the mainstem Shenandoah River. Based on the empirical bioaccumulation model and site-specific fish size, fish methylmercury, and water column total mercury levels, these target water column concentrations should be protective of the 0.3 ppm fish tissue methylmercury criterion. Accordingly, the mercury TMDLs were developed to meet these instream target water column concentrations.

While the empirical bioaccumulation model exhibited good overall fit, there are uncertainties associated with predicting restoration outcomes from such an empirical model. The model is based on existing conditions in the river, including methylation/demethylation rates, bioaccumulation rates, and existing food web structure. If these variables change in the future, the empirical relationship between total mercury in the water column and fish tissue methylmercury will likely change. The influence of stored mercury in bed sediments also adds to uncertainty in the exact trajectory of restoration. Due to these and other uncertainties, VADEQ anticipates implementing this TMDL using adaptive implementation strategies that will be flexible and responsive to new information (see Section 5.2).

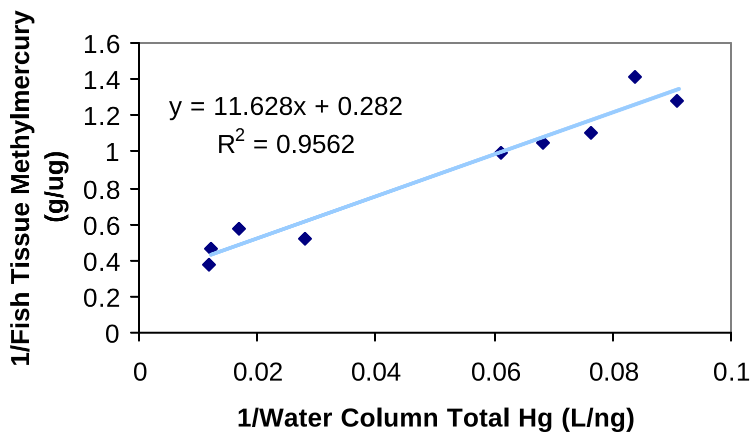



**Figure 2-12. Linearized Michaelis-Menten Inverse Plot of Size-normalized Smallmouth Bass Methylmercury Levels and Water Column Total Mercury Levels in the South River and South Fork Shenandoah River.**

**Table 2-3. Target Water Column Concentrations Protective of 0.3 ppm Fish Tissue Criterion.**

| River | Normalized Fish Size (g) | *a* | *b* | Target Water Column Concentration Protective of 0.3 ppm Fish Tissue Criterion (ng/L) |
|---|---|---|---|---|
| South River | 218 | 11.628 | 0.282 | 3.8 |
| South Fork Shenandoah River | 253 | 10.02 | 0.2429 | 3.2 |
| Shenandoah River | 321 | 7.8971 | 0.1915 | 2.5 |

#### *2.4.3.4. Evaluation of Alternative Empirical Relationships*

The relationship between total mercury in the water column and methylmercury in fish tissue was used to develop target water column concentrations for the South River mercury TMDL. An empirical bioaccumulation model in the form of the linearized Michaelis-Menten equation was used to describe this relationship. Other relationships and other models were also considered, but this combination produced the best empirical fit. Table 2-4 compares the $R^2$ values for other models and for relationships between fish tissue methylmercury and other water column constituents. Intuitively, other constituents in the water column such as methylmercury might be expected to better predict methylmercury concentrations in fish, however, these other relationships were not as strong as between total mercury in the water column and methylmercury in fish tissue.

**Table 2-4. Empirical Fit of Various Models Relating Water Column Mercury Levels to Methylmercury in Fish Tissue.**

| Constituent | Model Fit ($R^2$) | | |
|---|---|---|---|
| | Linear Model | Power Model | Michaelis-Menten Model |
| Total Mercury | 0.8865 | 0.9362 | **0.9562** |
| Dissolved Mercury | 0.5747 | 0.6527 | 0.7195 |
| Total Methylmercury | 0.6077 | 0.7121 | 0.8536 |
| Dissolved Methylmercury | 0.5092 | 0.5305 | 0.6625 |

# 3. SOURCE ASSESSMENT

Sources of mercury in the South River watershed include both point sources and nonpoint sources. Point sources include industrial and municipal wastewater treatment facilities, and nonpoint sources include atmospheric deposition, runoff from background or contaminated land surfaces, groundwater and interflow from background or contaminated land areas, and channel margin inputs. This section briefly summarizes source assessment information used in the development of the South River mercury TMDL model. More detailed information on the characterization and modeling of mercury sources is described in the USGS report in Attachment 1.

## 3.1. PERMITTED POINT SOURCES

There are 14 individually permitted point sources in the South River watershed (Table 3-1). Of those, only the industrial and major municipal facilities were included in the South River TMDL mercury model. Minor municipal facilities and water treatment facilities within the South River watershed were not sampled and were not included in the South River TMDL mercury model. None of these facilities are known or expected to be sources of mercury contamination, and the flows from these facilities are small enough that any measured mercury load would be insignificant. If the highest mercury concentration measured in municipal wastewater (7.6 ng/L measured in the Waynesboro STP discharge) were assumed for all of the minor municipal facilities and water treatment facilities, the combined mercury load from these discharges would be <0.005% of the existing mercury load in the South River.

In addition to individually permitted point sources, a number of general permits have been issued in the South River watershed. The number of each general permit type issued in the watershed is shown in Table 3-2. Similarly to minor municipal facilities, the general permits are not expected to be sources of mercury contamination, they are even smaller in flow, they contribute an insignificant load of mercury to the river, and therefore, they were not included in the South River TMDL mercury model.

**Table 3-1. Individually Permitted Discharges in the South River Watershed.**

| Facility Type | Permit No. | Facility Name | Outfall | Max Design Flow (MGD)[1] | River Mile | Receiving Stream |
|---|---|---|---|---|---|---|
| Industrial | VA0002160 | Invista | 001 | 5 | 25.3 | South River |
| | | | 003 | NA | 25.3 | South River |
| | | | 004 | NA | 25.3 | South River |
| | | | 006 | NA | 25.3 | South River |
| | | | 008 | NA | 25.3 | South River |
| | | | 009 | NA | 0.55 | South River, U.T. |
| | | | 010 | NA | 0.36 | South River, U.T. |
| | | | 011 | 0.386 | 25.17 | South River |
| | | | 012 | NA | 25.3 | South River |
| | | | 013 | NA | 25.3 | South River |
| | | | 014 | NA | 25.3 | South River |
| | VA0001767 | Alcoa Packaging LLC | 001 | 3.2 | 4.37 | South River |
| | VA0002402 | Former Genicom | 001 | 0.216 | 21.94 | South River |
| Major Municipal | VA0066877 | Stuarts Draft WWTP | 001 | 4 | 38.88 | South River |
| | VA0025151 | Waynesboro STP | 002[2] | 6 | 23.22 | South River |
| | | | 001 | 4 | 23.54 | South River |
| Minor Municipal | VA0027901 | Harriston STP | 001 | 0.1 | 8.2 | South River |
| | VA0028037 | Skyline Swannanoa | 001 | 0.15 | 2.96 | South River, U.T. |
| | VA0065374 | Grottoes STP | 001 | 0.4 | 1.59 | South River |
| | VA0088226 | Hugh K Cassell Elementary School | 001 | 0.011 | 0.35 | Porterfield Run, U.T. |
| | VA0067962 | Vesper View STP | 001 | 0.1 | 16.04 | South River |
| | VA0088943 | Blue Ridge MHC LLC | 001 | 0.024 | 14.2 | South River |
| | VA0023400 | DOC - Cold Springs Correctional Unit 10 | 001 | 0.06 | 1.99 | Poor Creek |
| | VA0088986 | Black Rock Mobile Home Park | 001 | 0.04 | 0.02 | South River, U.T. |
| Water Treatment | VA0092100 | Coyner Springs WTP | 001 | 0.414 | 1.29 | South River, U.T. |

[1] For industrial facilities, such as Invista, the listed flows are not maximum design flows, but represent the maximum monthly average flow that was used to develop permit limits for that outfall. For outfalls that contain only stormwater, the maximum design flow is listed as NA, or not applicable.
[2] This outfall will replace outfall 001 when wastewater treatment plant updgrades are completed.

For industrial and major municipal point sources that were included in the South River mercury model, discharge sampling for mercury was conducted to provide accurate model inputs. Since the former DuPont plant site was the original source of mercury to the river, a detailed monitoring program of mercury from this site was essential. As previously described (Section 2.2), DuPont continues to own the property, but the manufacturing assets, including the permitted discharge outfalls, are now owned by Invista. As a part of Resource Conservation and Recovery Act (RCRA) facility investigations, DuPont has conducted mercury monitoring of the Invista stormwater and wastewater outfalls since 2004 (Table 3-3). These data were used to characterize mercury inputs under existing condition scenarios as described in Attachment 1. While each Invista outfall was independently included in the South River model, flow and mercury monitoring results show that the majority of mercury load from the plant site is through outfalls 001, 011, and 008.

**Table 3-2. General Permits in the South River Watershed.**

| General Permit Type | # of Permits |
|---|---|
| Single Family Home | 9 |
| Industrial Stormwater | 16 |
| Ready-mix Concrete | 1 |
| Non-metallic Mineral Mining | 2 |
| Cooling Water | 1 |
| Land Application | 3 |
| Confined Animal Feeding Operation - Poultry | 10 |
| Confined Animal Feeding Operation - Dairy | 1 |

**Table 3-3. Mercury Monitoring at Invista Outfalls.**

| Outfall # | Outfall Description | Baseflow Hg Monitoring (ng/L)[1] | | Stormflow Hg Monitoring (ng/L)[1] | |
|---|---|---|---|---|---|
| | | Range | Average | Range | Average |
| 001 | Primary outfall for treated process wastewater and untreated non-process wastewater | 20 - 133 | 51 | 11 - 262 | 93 |
| 003 | Steam condensate, stormwater, Baker Spring and well water | 5 - 219 | 43 | 1 - 312 | 118 |
| 004 | Stormwater and well test water | 14 - 37 | 22 | 7 - 129 | 42 |
| 006 | Stormwater and well test water | 12 - 22 | 16 | 12 - 33 | 22 |
| 008 | Stormwater | 6 - 2492 | 222 | 21 - 591 | 190 |
| 009 | Stormwater | No baseflow | | 30 - 154 | 82 |
| 010 | Stormwater and well test water | No baseflow | | 87 - 449 | 238 |
| 011 | Untreated non-process wastewater and stormwater | 39 - 23808 | 2051 | 44 - 3400 | 889 |
| 012 | Stormwater | Not sampled; estimated from 010 results | | | |
| 013 | Overflow of consolidated sump internal outfall | Not sampled; estimated from 001 results | | | |
| 014 | Overflow of waste treatment sump | Not sampled; estimated from 001 results | | | |

[1] Summaries of mercury monitoring results represent outfall samples collected by DuPont from 11/2004 through 3/2007. DuPont has continued sampling, but additional data were not used in TMDL development

With the exception of the Invista discharge, no other point source discharges are known sources of mercury contamination to the South River. Due to their large flows or location within the contaminated flood plain, however, additional facilities could contribute measureable amounts of mercury to the river. For this reason, mercury loadings from all industrial and major municipal facilities were included in the South River TMDL mercury model. These industrial and major municipal point sources that were not expected to be significant sources of mercury were only sampled once to estimate mercury loadings (Table 3-4). Overall loads from these facilities were relatively small, but did exceed the protective instream target concentration of 3.8 ng/L at two facilities. Measured mercury concentrations in these discharges were used to characterize mercury inputs under existing condition scenarios as described in Attachment 1.

**Table 3-4. Mercury Concentrations Measured in Point Source Discharges.**

| Permit # | Facility Name | Sample Date | Mercury Concentration (ng/L) |
|---|---|---|---|
| VA0001767 | Alcoa Packaging LLC | 10/17/2006 | 18.3 |
| VA0002402 | Former Genicom | 10/17/2006 | 0.2 |
| VA0066877 | Stuarts Draft WWTP | 10/17/2006 | 0.7 |
| VA0025151 | Waynesboro STP | 10/17/2006 | 7.6 |

## 3.2. NONPOINT SOURCES

Nonpoint sources of mercury to the South River include atmospheric deposition, runoff from background or contaminated land surfaces, groundwater and interflow from background or contaminated land areas, and channel margin inputs. Attachment 1 describes how each of these sources was characterized in the South River mercury TMDL model. In general, initial estimates for each source were made based on available monitoring information. If necessary, those initial estimates were adjusted during the model calibration process to obtain agreement between simulation results and observed monitoring data. Table 3-5 shows the final model inputs for nonpoint sources.

**Table 3-5. Nonpoint Sources of Mercury to the South River.**

| Nonpoint Hg Source | Data Used to Determine Initial Concentrations | Model Input |
|---|---|---|
| Atmospheric deposition on river surface | USEPA (USEPA, 2007a) | Precip. concentration = 21.8 ng/L |
| Groundwater from uncontaminated land areas | $THG_F$ at Waynesboro gage (01626000) | Groundwater dissolved HG = 0.7 ng/L |
| Groundwater from HG contaminated flood plain | Flood-plain groundwater samples, plus calibration | Groundwater dissolved HG = 1.3 - 2.9 ng/L |
| Interflow | Precipitation $THG_F$ (USEPA, 2007a) and calibration | Calibrated values from 10.0 to 16.7 ng/L |
| Soil attached HG runoff from uncontaminated pervious and impervious land surfaces | Soil samples from uncontaminated areas | $THG_{Sed}$ = 0.07 ug/g for all uncontaminated HRUs |
| Soil attached HG runoff from contaminated pervious land surfaces | Soil samples within respective reaches | $THG_{Sed}$ concentration varies by reach and HRU from (7.6 to 16.7 ug/g) |
| Channel margin inputs | THG at Waynesboro (01626000), Dooms (01626920), and Harriston (01627500) | Calibrated values of sediment attached HG added to water column within each RCHRES |

# 4. TMDL DEVELOPMENT

The objective of a TMDL is to allocate allowable loads among different pollutant sources so that the appropriate control actions can be taken to achieve water quality standards (USEPA, 1991a). To achieve this objective, a water quality model was developed and calibrated to simulate existing conditions within the South River. Following successful calibration and simulation of existing conditions, future conditions were then projected, and various reduction scenarios were adjusted until water quality standards were met. Attachment 1 describes in detail the model development, calibration, and simulation of existing conditions, future conditions, and various allocation scenarios. This section briefly summarizes those results.

## 4.1. WATER QUALITY MODELING

The USGS developed a water quality model of the South River using the Hydrological Simulation Program-Fortran (HSPF) modeling platform. This water quality model simulates streamflow, sediment transport, and mercury transport in the South River. The hydrologic portion of HSPF generates time series of streamflow in response to precipitation, evapotranspiration, and movement of water from the land surface to stream networks through runoff, groundwater flow, and interflow. The sediment portion of HSPF simulates sediment loading from pervious and impervious land surfaces through washoff and scouring. Within the stream, HSPF simulates sediment transport, deposition, and resuspension. The mercury portion of the model simulates mercury loading from point sources, atmospheric deposition, runoff from background or contaminated land surfaces, groundwater and interflow from background or contaminated land areas, and channel margin inputs. Within the river, HSPF simulates mercury sorption/desorption to/from suspended particles, deposition and resuspension of sediment-associated mercury, and downstream advection. The USGS individually calibrated and verified the hydrologic, sediment transport, and mercury transport portions of the model with observed data to ensure that the model was effectively predicting instream flow, sediment, and mercury concentrations. Additional details of the South River mercury model are described in Attachment 1.

## 4.2. EXISTING CONDITIONS

Following calibration of the South River hydrologic, sediment, and mercury model, the model was used to simulate existing conditions. Existing conditions were simulated using weather and point source inputs for April 1, 2005 to March 31, 2007. Figure 4-1 and Figure 4-2 show simulated mercury concentrations in the South River under existing conditions. Mercury concentrations above the former DuPont plant site (at the Waynesboro gage) ranged from 0.6 to 53 ng/L, but 90-d median values were below the instream target of 3.8 ng/L. Within the contaminated reach (at Harriston) mercury concentrations ranged from 12 to over 5000 ng/L and were consistently well above the instream target. The median mercury concentration at Harriston was 91 ng/L under existing conditions, compared to 1.6 ng/L at Waynesboro.

Simulated results showed that mercury fluxes in the South River increased sharply from the former DuPont plant site downstream to Dooms and then stabilized (Figure 4-3). Mercury loadings above Waynesboro were relatively low (1 kg/yr). From Waynesboro to Hopeman Parkway, mercury loadings increased to 60 kg/yr. Loadings were highest in the reach from Hopeman Parkway to Dooms (87 kg/yr). Below Dooms, mercury loadings decreased, with 36 kg/yr entering the reach ending at Harriston and only 6 kg/yr entering the reach ending at Port Republic. These simulation results are consistent with other findings of the SRST that the majority of mercury loadings to the South River occur from the former DuPont plant site to Dooms.

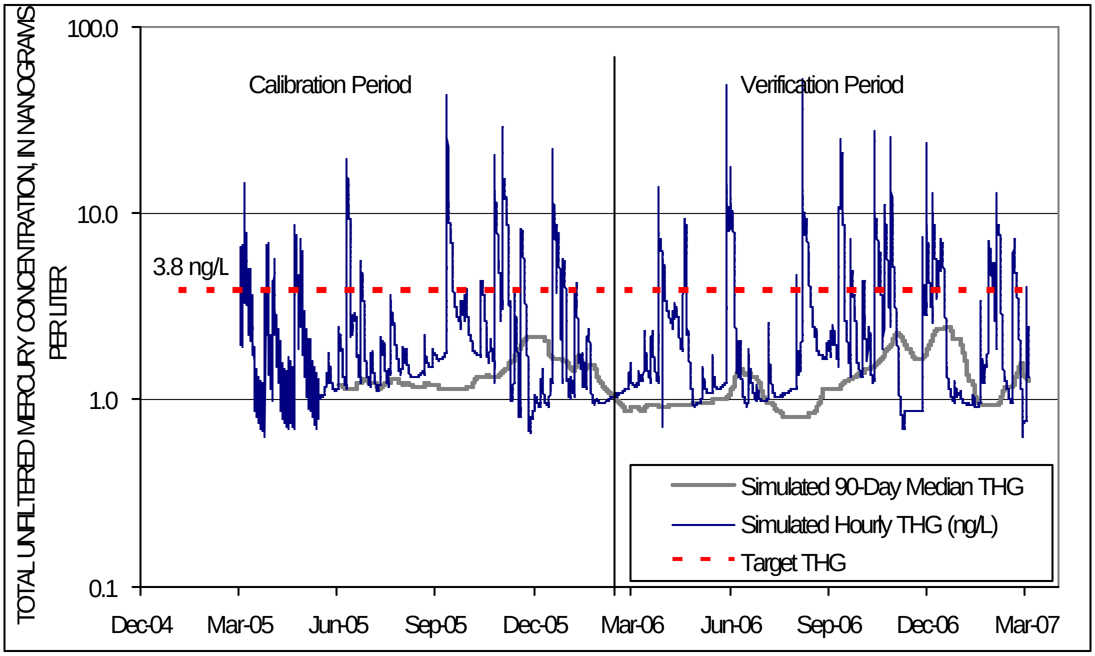



**Figure 4-1. HSPF Model Simulation of Mercury Concentrations in the South River at Waynesboro Under Existing Conditions (April 2005 - April 2007).**

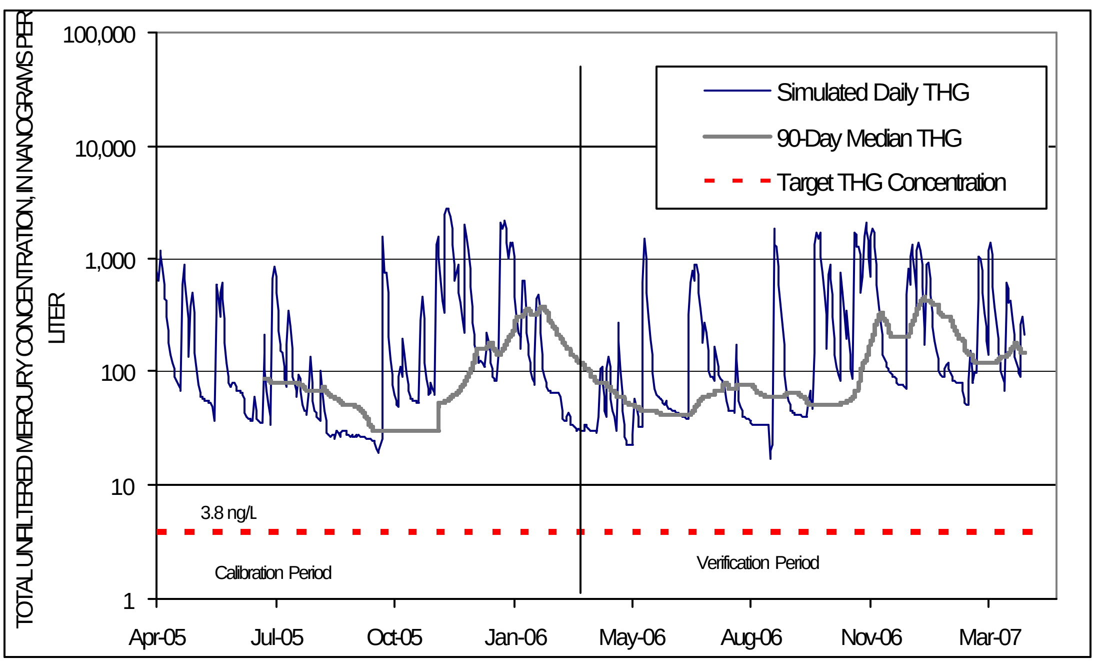



**Figure 4-2. HSPF Model Simulation of Mercury Concentrations in the South River at Harriston Under Existing Conditions (April 2005 – April 2007).**

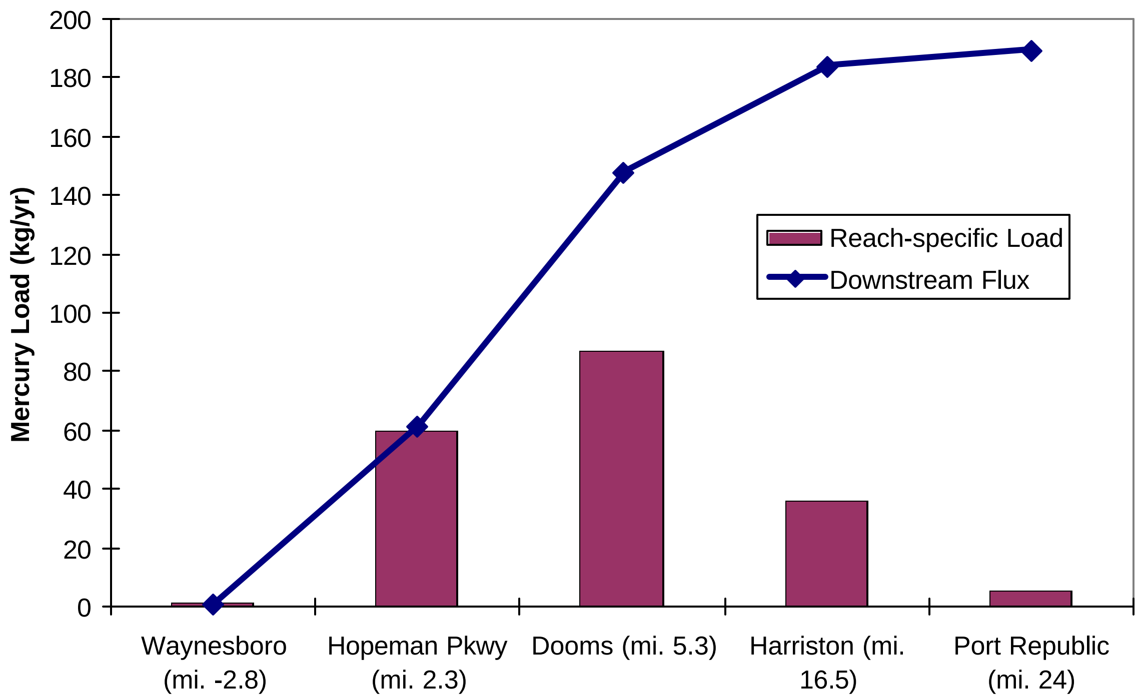



**Figure 4-3. Mercury Loadings and Downstream Flux in the South River.**

The sources of mercury loadings to the South River under existing conditions are shown in Figure 4-4. The majority of mercury (84%) was determined to be from channel margin inputs, which include bank erosion, disturbance, collapse, or other mechanisms that can transfer mercury contaminated material from the contaminated channel margins to the water column or river bed. The second most prevalent mercury source (at 15%) was sediment-attached mercury carried in runoff from the land surface. This includes a small portion from naturally occurring or atmospherically deposited mercury from uncontaminated areas (4%), but primarily represents mercury from the contaminated flood plain (96%). All other sources were relatively small with respect to annual loadings, however, their contribution can have a significant impact on daily water column concentrations of mercury. For instance, point sources contributed only 0.34% of annual average mercury loads, but reduction scenarios that reduced point source concentrations to 3.8 ng/L reduced median simulated mercury concentrations in the river by as much as 14%. In addition, reductions in channel margin and runoff sources of mercury alone were insufficient to meet TMDL targets. Reductions from point sources were required, even though total annual loading from those sources are small in comparison to other sources.

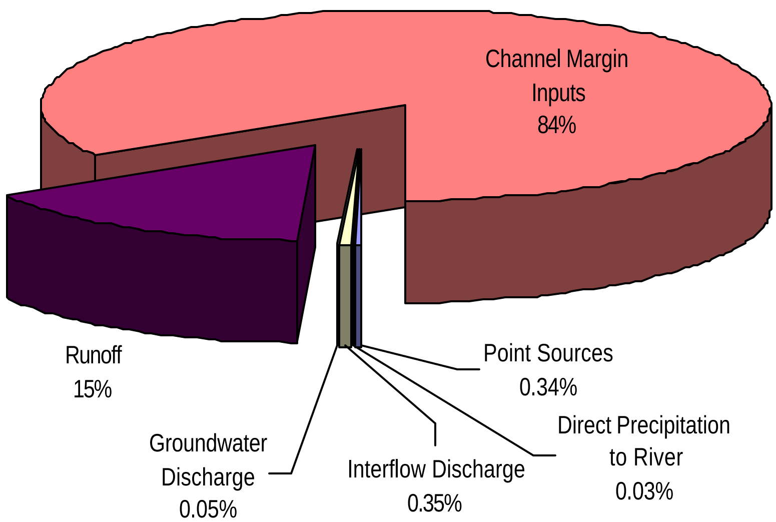



**Figure 4-4. Source Contributions of Mercury to the South River Under Existing Conditions.**

## 4.3. ALLOCATION SCENARIOS

Following calibration and evaluation of the South River mercury model under existing conditions, various future reduction scenarios were simulated to determine the level of reductions needed to meet instream water quality targets. Table 4-1 shows the various scenarios that were simulated. The results of each scenario are described in detail in Attachment 1. In general, none of the scenarios were successful in meeting the instream water quality target except for Scenario 4B. This scenario became the TMDL allocation scenario for the South River.

**Table 4-1. Simulated Allocation Scenarios for Mercury in the South River.**

| Scenario Type | Scenario # | Scenario Conditions |
|---|---|---|
| Existing conditions | 1 | Calibrated model under existing conditions;<br>All current mercury loads included |
| Future conditions | 2 | Point source flows increased to maximum permitted or design flows;<br>Invista outfall 011 directed to the South River;<br>Precipitation and interflow mercury inputs reduced by 19% |
| Single source reductions | 3A | All future conditions in effect;<br>Point source concentrations reduced to target instream concentration (3.8 ng/L) |
| | 3B | All future conditions in effect;<br>Channel margin inputs reduced by 100% |
| | 3C | All future conditions in effect;<br>Runoff cleaned to background conditions (reduced by 96%) |
| Multiple source reductions | 4A | All future conditions in effect;<br>Channel margin inputs reduced by 100%;<br>Runoff cleaned to background conditions (reduced by 96%) |
| | 4B (TMDL Scenario) | All future conditions in effect;<br>Channel margin inputs reduced by 100%;<br>Runoff cleaned to background conditions (reduced by 96%)<br>Point source concentrations reduced to target instream concentration (3.8 ng/L) |

## 4.4. SOUTH RIVER TMDL

A TMDL considers all sources contributing mercury to the South River, including point (or direct) and nonpoint (or indirect) sources. The TMDL can be shown to represent these sources as defined in the following equation:

$$TMDL = WLA + LA + MOS \qquad [4\text{-}1]$$

Where,

WLA = wasteload allocation (point source contributions),

LA = load allocation (nonpoint source contributions), and

MOS = margin of safety.

The objective of the mercury TMDL for the South River is to determine what reductions in mercury loadings from point and nonpoint sources are required to meet state water quality standards. As described in Section 2.4, the applicable water quality standard is a fish tissue methylmercury concentration of 0.3 ppm, and the instream water quality target to achieve this goal was determined to be a 90-d median mercury concentration of 3.8 ng/L in the water column. Allocation scenario 4B successfully met this criterion and was selected as the TMDL allocation scenario. This scenario calls for an overall 99% reduction in mercury loadings from existing conditions (Table 4-2). Under this reduction scenario, the average annual mercury load at the outlet of the South River is 2,029 g/yr. This is the annual expression of the mercury TMDL for the South River.

The TMDL scenario includes elimination of channel margin inputs, a 96% reduction from runoff, an 83% reduction from point sources, and a 19% reduction from interflow and direct precipitation. The 83% point source reduction represents all point sources reducing mercury concentrations in the discharge to 3.8 ng/L. The 96% reduction in runoff loading represents returning flood plain soils to background mercury levels of 0.07 ug/g on average. The 19% reduction in interflow and direct precipitation represents the predicted reductions achieved through USEPA's Clean Air Interstate Rule and the Clean Air Mercury Rule.

**Table 4-2. Mercury Load Reductions Necessary to Meet TMDL Conditions in the South River.**

| Source | Annual Hg Loading Under Existing Conditions (g/yr) | Annual Hg Loading Under TMDL Conditions (g/yr) | Percent Reduction (%) |
|---|---|---|---|
| Point Sources | 650 | 112 | 83% |
| Direct Precipitation to River | 55 | 45 | 19% |
| Interflow | 667 | 558 | 19% |
| Groundwater | 99 | 99 | 0% |
| Runoff | 29,237 | 1,216 | 96% |
| Channel Margin | 158,713 | 0 | 100% |
| **Total** | **189,421** | **2,029** | **99%** |

### 4.4.1. Wasteload Allocations

Wasteload allocations quantify the amount of mercury allowed in point source discharges under the TMDL scenario. Table 4-3 shows the wasteload allocations for industrial and major municipal facilities in the South River watershed. As described in Section 3.1, minor municipal facilities and facilities covered under general discharge permits are considered insignificant sources of mercury and were not assigned wasteload allocations.

Calculated wasteload allocations were expressed as an average annual load, an average daily load, and a maximum daily load. All three expressions are consistent with the TMDL scenario described above (scenario 4B). In this scenario, point sources were modeled as discharging continuously at the maximum design flow and instream water quality target of 3.8 ng/L. Based on this scenario, the annual expression of the wasteload allocation was calculated by multiplying the maximum design flow of each facility by the instream water quality target (and appropriate unit conversions) and summing the calculated loads for a year. The average daily expression of the wasteload allocation was then calculated by dividing the annual allocation by 365. The maximum daily expression of the wasteload allocation was statistically derived to define the allowable variability around average daily loads that would be protective of the annual allocation. The following formula from USEPA's *Technical Support Document for Water Quality-Based Toxics Control* (USEPA, 1991b) and USEPA's draft *Options for Expressing Daily Loads in TMDLs* (USEPA, 2007b) was used to calculate maximum daily wasteload allocations for each facility.

$$MDL = LTA * \exp(Z_p s_y - 0.5 s_y^2) \qquad [4\text{-}2]$$

Where,

$MDL$ = Maximum daily load,

$LTA$ = Long term average, which in this case is the average daily load,

$Z_p$ = $p^{th}$ percentage point of the standard normal distribution (95th percentile was used),

$s_y = \sqrt{\ln(CV^2 + 1)}$ , and

$CV$ = Coefficient of variation (estimated at 0.6 for each facility).

Wasteload allocations for continuous discharges were calculated as described above. The wasteload allocation for Invista's stormwater discharges was calculated differently. Because the TMDL scenario calls for clean up of flood plain areas to background levels, the wasteload allocation for stormwater discharges was based on the modeled runoff loads from an uncontaminated area with similar landuse. An annual lumped allocation for Invista's stormwater discharges was calculated as the mercury runoff load from 113 acres of high intensity impervious urban landuse modeled during the 2-yr TMDL simulation period, divided by 2. The daily average wasteload allocation was then calculated as the annual load divided by 365. The maximum daily wasteload allocation was determined as the 95th percentile of modeled daily loads from this land area during the 2-yr TMDL simulation period.

**Table 4-3. Mercury Wasteload Allocations in South River TMDL.**

| Permit No | Facility Name | Outfall | Max Design Flow (MGD)[1] | Target Hg Conc. (ng/L) | Wasteload Allocation | | |
|---|---|---|---|---|---|---|---|
| | | | | | Annual (g/yr) | Average Daily (g/d) | Maximum Daily (g/d) |
| VA0002160 | Invista[2] | 001 | 5 | 3.8 | 26 | 0.072 | 0.15 |
| | | 011 | 0.386 | 3.8 | 2.0 | 0.0056 | 0.012 |
| | | Combined stormwater flow | NA | NA | 13 | 0.036 | 0.11 |
| | | | | Subtotal | 41 | 0.114 | 0.27 |
| VA0001767 | Alcoa Packaging LLC | 001 | 3.2 | 3.8 | 17 | 0.046 | 0.10 |
| VA0002402 | Former Genicom | 001 | 0.216 | 3.8 | 1.1 | 0.0031 | 0.007 |
| VA0066877 | Stuarts Draft WWTP | 001 | 4 | 3.8 | 21 | 0.058 | 0.12 |
| VA0025151 | Waynesboro STP | 002 | 6 | 3.8 | 31 | 0.086 | 0.18 |
| | | | | **Total** | **112** | **0.306** | **0.69** |

[1] For industrial facilities, such as Invista, the listed flows are not maximum design flows, but represent the maximum monthly average flow that was used to develop permit limits for that outfall. For outfalls that contain only stormwater, the maximum design flow is listed as NA, or not applicable.

[2] The wasteload allocations for outfall 001 and 011 represent the non-stormwater flows from these outfalls. The allocation for all stormwater flows (regardless of the outfall) are collectively represented in the row titled "Combined stormwater flow".

### 4.4.2. Load Allocation

The load allocation (LA) portion of the South River mercury TMDL represents the contributions of mercury from all nonpoint sources. The annual load allocation was calculated as the sum of modeled loads from all nonpoint sources under the TMDL scenario during the 2-yr simulation period, divided by 2. As described above, the TMDL scenario includes elimination of channel margin inputs, a 96% reduction from runoff, and a 19% reduction from interflow and direct precipitation. Based on these reductions, the annual LA was calculated as 1917 g/yr. For daily expressions of the LA (on an average daily basis or a maximum daily basis), the LA was calculated as the difference of the TMDL and the WLA.

### 4.4.3. Margin of Safety

In the South River mercury TMDL, an implicit margin of safety (MOS) was included. Implicit margins of safety are implemented by using conservative estimates of model input parameters and by using a conservative calibration of water quality parameters. Specific conservative assumptions used in the South River mercury TMDL are described below:

- The empirical bioaccumulation model used to develop the protective instream water quality target was based only on smallmouth bass, the highest trophic level consumer in the South River aquatic food web and the most contaminated fish species. Other fish species that may be consumed by anglers would reach safe levels (<0.3 ppm methylmercury) under reduction scenarios less stringent than the TMDL scenario.

- The use of a non-linear empirical bioaccumulation model provided a more conservative estimate of protective instream water quality targets than the traditional bioaccumulation factor approach. Using the traditional bioaccumulation factor approach (i.e., estimating protective instream water quality targets based on a simple ratio of fish tissue to water column mercury levels at the site), site-specific water quality targets would have ranged from 4.4 to 11.6 ng/L at South River sites rather than the 3.8 ng/L target estimated from the non-linear empirical bioaccumulation model.

- Under the TMDL scenario, point sources were modeled at maximum permitted flow rates for all facilities. While some facilities will likely expand in the future, the likelihood of all facilities reaching their maximum flow rates is small. Average flows from these facilities under existing conditions represented only 27% to 70% of maximum design flows.

- The mercury model was calibrated conservatively, such that error between simulated and observed values was generally in the direction of over prediction. For instance, high end total mercury concentrations, which occur during storms, were simulated higher than the highest observed total mercury concentrations.

### 4.4.4. TMDL Expressions

The mercury TMDL in the South River is designed to protect human health from mercury exposure through fish consumption. The accumulation of mercury in fish tissue is reflective of exposure over extended time periods, ranging from seasonal to annual. Similarly, human health effects from mercury typically result from long term exposures. Consequently, the most relevant expression of mercury loadings in the South River TMDL is the annual average loading. Table 4-4 shows the South River mercury TMDL expressed as an average annual load. This TMDL represents the sum of mercury loadings to the South River under the TMDL scenario (4B) for the 2-yr simulation period, divided by 2.

**Table 4-4. Total Maximum Daily Load of Mercury for the South River Expressed as an Average Annual Load.**

| Stream | WLA (g/yr) | LA (g/yr) | MOS | TMDL (g/yr) |
|---|---|---|---|---|
| South River | 112 | 1917 | Implicit | 2029 |

In order to comply with current USEPA guidance (USEPA, 2007b), the South River mercury TMDL was also expressed as a daily load in two ways. First, the TMDL was expressed as an average daily load by dividing the average annual load by 365 (Table 4-5). This average daily load represents conditions that, if maintained consistently, would meet the annual loading. Loading conditions, however, are not consistent and are largely influenced by storm events. For this reason, the daily load was also expressed as a daily maximum by evaluating the variability and distribution of simulated daily loads (Table 4-6). The maximum daily load was determined from Equation 4-2 using a 95$^{th}$ percentile and a CV calculated from the mean and standard deviation of simulated daily loads. This calculated maximum daily load of 21.50 g/d was relatively consistent with the empirical 95$^{th}$ percentile of simulated daily loads (18.20 g/d). It should be noted that the maximum daily load expression represents extreme conditions (with a 5% frequency of occurrence), and routine loadings of this level would not meet average annual loadings that are necessary to protect human health and maintain fish tissue levels below 0.3 ppm methylmercury.

**Table 4-5. Total Maximum Daily Load of Mercury for the South River Expressed as an Average Daily Load.**

| Stream | WLA (g/d) | LA (g/d) | MOS | TMDL (g/d) |
|---|---|---|---|---|
| South River | 0.306 | 5.256 | Implicit | 5.562 |

**Table 4-6. Total Maximum Daily Load of Mercury for the South River Expressed as a Maximum Daily Load.**

| Stream | WLA (g/d) | LA (g/d) | MOS | TMDL (g/d) |
|---|---|---|---|---|
| South River | 0.69 | 20.81 | Implicit | 21.50 |

## 4.5. SOUTH FORK SHENANDOAH AND SHENANDOAH RIVER TMDLS

The mercury impairment that originates in the South River extends downstream for 156 miles and includes the South Fork Shenandoah River and portions of the North Fork Shenandoah River and Shenandoah River. For this reason, TMDLs were also developed for the South Fork Shenandoah River and the Shenandoah River. No TMDL was developed for the small impaired portion of the North Fork Shenandoah River, because the listing of this segment was not based on mercury contamination in the North Fork Shenandoah River but on the possibility of fish movement upstream from the contaminated South Fork Shenandoah River. The implementation of TMDLs and the removal of impairments in the South River, South Fork Shenandoah, and Shenandoah Rivers would also mean the removal of the North Fork Shenandoah River mercury impairment.

Mercury TMDLs in the South Fork Shenandoah and Shenandoah Rivers were developed using a simple mixing model. This mixing model calculated resulting mercury concentrations in the South Fork Shenandoah and Shenandoah Rivers based on mathematically mixing the South River HSPF model output with flow from uncontaminated tributaries to achieve the gaged flow in these rivers. Contributions from uncontaminated tributaries were modeled at 1.81 ng/L, which was the average concentration measured in the North River, an uncontaminated tributary of the South Fork Shenandoah River. Attachment 1 describes the mixing model development and results in more detail.

Results from the South Fork Shenandoah River and Shenandoah River mixing models show that TMDL reductions in the South River will allow downstream rivers to meet the applicable instream water quality targets without further reductions. Figure 4-5 and Figure 4-6 show the successful TMDL scenarios for the South Fork Shenandoah River and Shenandoah River, respectively.

The TMDLs for these downstream rivers were calculated by summing the loads from the mixing model over the 2-yr simulation period, and dividing by 2. Daily average and daily maximum expressions of the TMDL were calculated as described for the South River. Wasteload allocations were equivalent to the wasteload allocations in the South River TMDL, since no additional dischargers on downstream rivers were considered to be significant sources of mercury. The load allocation was calculated as the difference of the TMDL and WLA. Like the South River TMDL, an implicit margin of safety was used. Table 4-7, Table 4-8, and Table 4-9 show the South Fork Shenandoah River and Shenandoah River TMDLs expressed as average annual loads, average daily loads, and maximum daily loads, respectively.

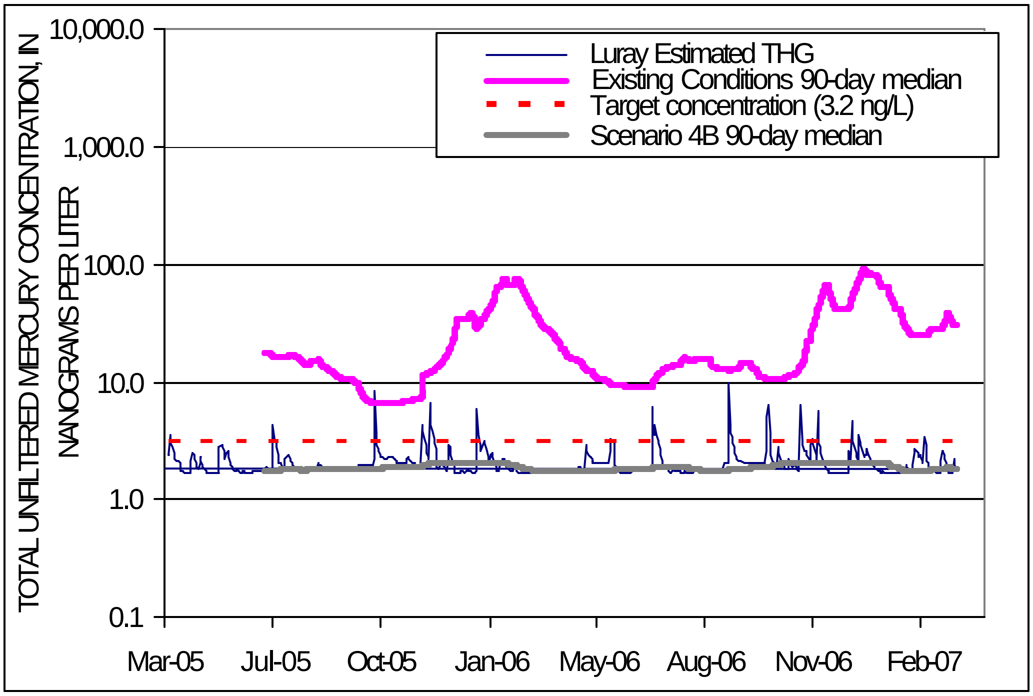



**Figure 4-5. Existing Condition and TMDL Scenario for South Fork Shenandoah River.**

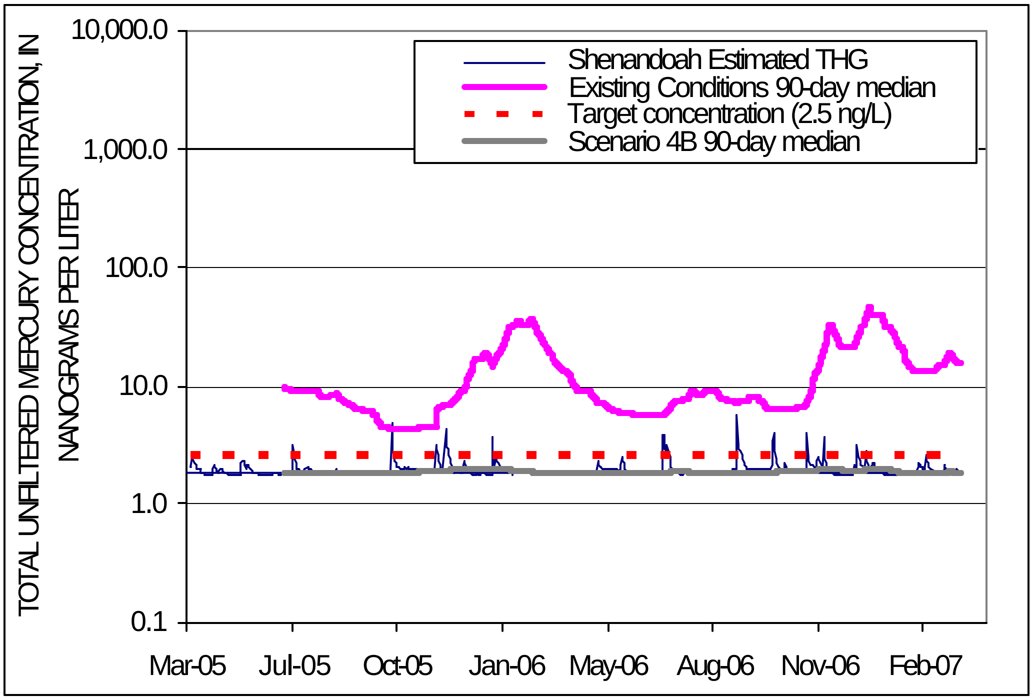



**Figure 4-6. Existing Condition and TMDL Scenario for Shenandoah River.**

**Table 4-7. Total Maximum Daily Load of Mercury for the South Fork Shenandoah River and Shenandoah River Expressed as an Average Annual Load.**

| Stream | WLA (g/yr) | LA (g/yr) | MOS | TMDL (g/yr) |
|---|---|---|---|---|
| South Fork Shenandoah River | 112 | 4008 | Implicit | 4120 |
| Shenandoah River (at Craigs Run) | 112 | 5948 | Implicit | 6060 |

**Table 4-8. Total Maximum Daily Load of Mercury for the South Fork Shenandoah River and Shenandoah River Expressed as an Average Daily Load.**

| Stream | WLA (g/d) | LA (g/d) | MOS | TMDL (g/d) |
|---|---|---|---|---|
| South Fork Shenandoah River | 0.306 | 10.982 | Implicit | 11.288 |
| Shenandoah River (at Craigs Run) | 0.306 | 16.297 | Implicit | 16.603 |

**Table 4-9. Total Maximum Daily Load of Mercury for the South Fork Shenandoah River and Shenandoah River Expressed as a Maximum Daily Load.**

| Stream | WLA (g/d) | LA (g/d) | MOS | TMDL (g/d) |
|---|---|---|---|---|
| South Fork Shenandoah River | 0.69 | 41.39 | Implicit | 42.08 |
| Shenandoah River (at Craigs Run) | 0.69 | 57.21 | Implicit | 57.90 |

# 5. TMDL IMPLEMENTATION AND REASONABLE ASSURANCE

Once a TMDL has been approved by USEPA, measures must be taken to reduce pollution levels from both point and nonpoint sources. The following sections outline the framework used in Virginia to provide reasonable assurance that the required pollutant reductions can be achieved.

## 5.1. CONTINUING PLANNING PROCESS AND WATER QUALITY MANAGEMENT PLANNING

As part of the Continuing Planning Process, VADEQ staff will present both USEPA-approved TMDLs and TMDL implementation plans to the State Water Control Board (SWCB) for inclusion in the appropriate Water Quality Management Plan (WQMP), in accordance with the Clean Water Act's Section 303(e) and Virginia's Public Participation Guidelines for Water Quality Management Planning.

VADEQ staff will also request that the SWCB adopt TMDL WLAs as part of the Water Quality Management Planning Regulation (9VAC 25-720), except in those cases when permit limitations are equivalent to numeric criteria contained in the Virginia Water Quality Standards, such as in the case of bacteria. This regulatory action is in accordance with §2.2-4006A.4.c and §2.2-4006B of the Code of Virginia. SWCB actions relating to water quality management planning are described in VADEQ's public participation guidelines (VADEQ, 2004), which can be found on VADEQ's web site at: http://www.deq.state.va.us/tmdl/pdf/ppp.pdf.

## 5.2. ADAPTIVE IMPLEMENTATION STRATEGY

VADEQ intends to implement this TMDL using an adaptive implementation strategy. Adaptive implementation is an iterative implementation process that makes progress toward achieving water quality goals while using new data and information to reduce uncertainty and adjust implementation activities (Wong, 2006). This approach is particularly useful for the South River mercury TMDL because of the complexities and uncertainties involved in understanding mercury cycling in the South River system. An adaptive implementation strategy allows responsiveness to new information and understanding, and it provides for needed flexibility in implementing the TMDL.

### 5.2.1. Responsiveness to New Information and Understanding

In 2000, the South River Science Team (SRST) was formed to address technical and scientific aspects of mercury behavior in the South River. The SRST consists of various partners including DuPont and DuPont contractors, VADEQ, Virginia Department of Game and Inland Fisheries, VDH, USEPA, U.S. Fish and Wildlife Service, local environmental groups, and numerous universities and research organizations. Throughout the years, SRST members have conducted numerous studies that have added to the growing understanding of mercury in the South River system. As new information and understanding continue to be developed, implementation efforts should be adaptable enough to take advantage of those advances.

While adaptive implementation is not anticipated to lead to perpetual re-opening of the TMDL, the TMDL and allocation scenarios can be modified in the future if warranted by significant new data or information. The TMDL, as developed, provides the best estimate of necessary mercury source reductions, based on the current understanding of mercury in the South River. If that understanding significantly changes in the future, TMDL modifications may be warranted. Two areas of particular research need are listed below.

- <u>Channel margin sources</u> – The largest source of mercury loading under existing condition simulations was attributed to the channel margins. Parallel loading studies conducted by SRST members have come to similar conclusions, however, these channel margin sources are not well-defined or delineated. Future studies of channel margin sources will be important in advancing the understanding of mercury loading in the South River.

- <u>Mercury methylation and trophic transfer</u> – The empirical bioaccumulation model used in this TMDL to establish protective instream water column concentrations of mercury is based on the current observed relationships between mercury in the water column and methylmercury in fish. Embedded within this empirical relationship are the complex processes of mercury methylation and trophic transfer. If these processes are altered in the system, which is a potential implementation strategy, the empirical relationship and resulting protective instream concentrations would also change. These changes could have a large impact on necessary mercury source reductions. Improved understanding of these processes could also lead to more explicit inclusion of them in South River modeling efforts.

Significant developments that fundamentally change our understanding of the above two areas, for example, may warrant reevaluation of current TMDL assumptions. New data in other less critical areas may not warrant reevaluation of the TMDL, but will still be considered in implementation planning. For example, since the calibration of the South River mercury TMDL model, new data sets of mercury levels in flood plain soils have been developed. These new data provide a much more comprehensive picture of mercury distribution within the flood plain, but do not differ dramatically from TMDL assumptions and do not fundamentally alter our understanding of flood plain mercury. This information, however, may be valuable in evaluating potential remedial options.

### 5.2.2. Flexibility in Implementing the TMDL

An adaptive implementation approach will allow needed flexibility in exploring, evaluating, and implementing mercury remediation strategies. While the TMDL formally focuses only on mercury source reductions, other avenues of remediation and control will be considered in implementation planning. These options may include treatments or manipulations to reduce bioavailability, interrupt or slow methylation processes, alter trophic transfer, or otherwise cut-off mercury pathways. Implementation of these approaches will require considerable experimentation and pilot testing, but their inclusion in implementation planning will likely be necessary. TMDL modeling shows that complete reliance on mercury source reductions alone will mean meeting extremely large and difficult to achieve reduction levels (99%). A successful implementation plan will likely employ a combination of mercury source controls as well as innovative approaches that influence mercury pathways.

### 5.2.3. Measures of Success

The mercury TMDL provides a framework for estimating the magnitude of mercury source reductions necessary to restore fish consumption uses. While implementation planning will target those reduction levels, the success of the TMDL will not be measured in mercury loading reductions. The ultimate measure of implementation success will be the resulting methylmercury concentrations in fish from the South River, South Fork Shenandoah River, and Shenandoah River. Any remedial strategies that can impact fish methylmercury levels may be considered in implementation planning.

## 5.3. IMPLEMENTATION OF WASTE LOAD ALLOCATIONS

To implement the WLA component of the TMDL, Virginia utilizes the National Pollutant Discharge Elimination System (NPDES) program administered by the Commonwealth under authority delegated by the USEPA. Federal regulations require that all new or revised NPDES permits be consistent with the assumptions and requirements of any applicable TMDL WLA (40 CFR §122.44 (d)(1)(vii)(B)). These regulations allow permits to use best management practices (BMPs) in lieu of numeric effluent limitations under certain conditions (40 CFR 122.44(k)). These conditions include where "[n]umeric effluent limitations are infeasible; or [t]he practices are reasonably necessary to achieve effluent limitations and standards or to carry out the purposes and intent of the CWA."

The Commonwealth of Virginia intends to use non-numeric permit requirements to comply with the WLA provisions of the TMDL. In this case, BMPs have been determined to be appropriate and reasonably necessary to achieve water quality standards and to carry out the goals of the TMDL. This approach will entail additional data collection from those facilities assigned a WLA in the TMDL. The additional data collection will better characterize the magnitude and variability of mercury dischargers. Where warranted, BMPs will be implemented through the development and execution of a Pollutant Minimization Plan. Associated BMPs are intended to focus on mercury source tracking and eliminating mercury at its source, rather than end-of-pipe controls; however treatment approaches may be applicable in certain circumstances.

Following USEPA approval of the South River mercury TMDL, VADEQ will reevaluate the permits for facilities with assigned mercury WLAs for inclusion of additional requirements that will ensure compliance with the established WLAs. Reopened or reissued permits should include the following provisions:

- Additional monitoring of mercury using low-level detection techniques (Method 1631) should be conducted. The frequency of testing, quality control requirements, and specific sampling conditions (such as flow) should be prescribed in the permit.

- If the results of monitoring indicate actual or potential exceedance of the protective instream water quality target (3.8 ng/L) or the wasteload allocation specified in the approved TMDL, the permittee would be required to submit for review and approval a Pollutant Minimization Plan (PMP). The plan would be designed to locate and reduce mercury sources to the discharge. The permittee would be required to execute and periodically update the plan until monitoring and/or compliance with approved BMPs demonstrate that the assigned wasteload allocation is consistently met.

Regulatory compliance with the mercury provisions given above would not be based on meeting a specific numeric limit. Through implementing the above provisions, however, there is the expectation that discharged mercury loads would decrease and ultimately meet the assigned numeric wasteload allocations. Regulatory compliance with the mercury provisions of the TMDL would be based on successfully fulfilling the relevant permit requirements, including additional monitoring and development and execution of a PMP, if necessary.

## 5.4. IMPLEMENTATION OF LOAD ALLOCATIONS

The TMDL program does not impart new implementation authorities. Therefore, the Commonwealth intends to use existing programs to the fullest extent in order to attain its water quality goals. In general, implementation measures for point sources are established through the NPDES permit program. Measures for nonpoint source reductions are implemented in an iterative process that is described in the TMDL implementation plan.

### 5.4.1. Implementation Plan Development

For the implementation of the TMDL's LA component, a TMDL implementation plan will be developed that addresses at a minimum the requirements specified in the Code of Virginia, Section 62.1-44.19.7. Virginia's 1997 Water Quality Monitoring, Information and Restoration Act (the "Act") directs the SWCB to "develop and implement a plan to achieve fully supporting status for impaired waters". The Act also establishes that the implementation plan "shall include the date of expected achievement of water quality objectives, measurable goals, corrective actions necessary and the associated costs, benefits and environmental impacts of addressing the impairments". USEPA outlines the minimum elements of an approvable implementation plan in its 1999 "Guidance for Water Quality-Based Decisions: The TMDL Process" (USEPA, 1999). The listed elements include implementation actions/management measures, timelines, legal or regulatory controls, time required to attain water quality standards, monitoring plans and milestones for attaining water quality standards.

In order to qualify for other funding sources, such as USEPA's Section 319 grants, additional plan requirements may need to be met. The detailed process for developing an implementation plan has been described in the "TMDL Implementation Plan Guidance Manual", published in July 2003 (VADCR, 2003) and available upon request from the VADEQ and VADCR TMDL project staff or at http://www.deq.virginia.gov/tmdl/implans/ipguide.pdf. This guidance was not designed specifically for the implementation of mercury TMDLs, but it can provide a useful framework for developing the plan.

The difficulties and complexities of implementing a mercury TMDL will necessitate additional flexibility in the implementation planning. As described above (Section 5.2.2), mercury source reductions alone will likely not be sufficient to cost-effectively restore the fish consumption use. Additional innovative strategies that reduce bioavailability, interrupt or slow methylation processes, alter trophic transfer, or otherwise cut-off mercury pathways will likely be needed and will be considered throughout implementation plan development. Since these innovative approaches are not well established, the initial stages of TMDL implementation may include additional data collection, research, and testing. In fact, some of these tasks have already begun. With the support of the SRST, DuPont has formed a Remedial Options Team and initiated a Remedial Options Program. This team has begun and will continue to investigate traditional, as well as, innovative remediation techniques. A pilot bank stabilization project initiated by the team is currently underway. VADEQ anticipates that a successful implementation plan will likely contain a combination of treatment technologies, source removal, source controls, BMPs, administrative controls, and innovative strategies that interrupt mercury pathways.

Watershed stakeholders will have opportunities to provide input and to participate in the development of the TMDL implementation plan. Regional and local offices of VADEQ, VADCR, the Virginia Department of Game and Inland Fisheries, other cooperating agencies, and the SRST will provide technical resources to assist in this endeavor.

With successful completion of implementation plans, local stakeholders will have a blueprint to restore impaired waters and enhance the value of their land and water resources. Additionally, development of an approved implementation plan may enhance opportunities for obtaining financial and technical assistance during implementation.

### 5.4.2. Link to Ongoing Restoration Efforts

Other ongoing water (and air) quality improvement efforts will contribute to the implementation of this mercury TMDL. A summary of those efforts are provided below:

- Virginia's Water Clean-up Plan – In 2006, the Virginia General Assembly passed legislation requiring the Secretary of Natural Resources to develop a plan for the clean up of the Chesapeake Bay and Virginia's waters (HB 1150). This plan (Commonwealth of Virginia, 2007) addresses both point and nonpoint sources of pollution and includes measureable and attainable objectives for water clean up, attainable strategies, a specified timeline, funding sources, and mitigation strategies. Additionally, challenges to meeting the clean-up plan goals (i.e., lack of program funding, staffing needs, monitoring needs) are identified. Information regarding Virginia's Water Clean-up Plan can be found at http://www.naturalresources.virginia.gov/Initiatives/WaterClean-upPlan/.

- Chesapeake Bay Nutrient and Sediment Tributary Strategy – In 2005, the Secretary of Natural Resources developed tributary strategies for the major basins discharging to the Chesapeake Bay (VASNR, 2005). These strategies set nutrient and sediment reductions for the basins and highlight practices to achieve those reductions. Many of the BMPs that will be used to reduce nutrients and sediment contributions as part of the Potomac River Basin Tributary Strategy will also reduce mercury loads to the South River. Since the majority of mercury entering the river is attached to sediments, reductions in sediment from the contaminated flood plain will also reduce mercury loadings. More information on the Potomac Basin Tributary Strategy can be found at: http://www.naturalresources.virginia.gov/Initiatives/WaterQuality/FinalizedTribStrats/shenandoah.pdf.

- Air Quality Regulations – The USEPA promulgated the Clean Air Interstate Rule (CAIR) in 2005. This legislation will reduce emissions of air pollutants, including mercury, by 2015. In addition, the Clean Air Mercury Rule (CAMR) was promulgated to specifically cap and reduce mercury emissions. These rules are estimated to result in a 19% reduction in mercury deposition within the South River watershed. While the overall contribution of atmospheric mercury to the South River impairment is small, the anticipated 19% reduction is included in the TMDL scenario.

- Natural Resources Defense Council (NRDC)/Sierra Club Settlement Agreement – In 2005, DuPont entered into a settlement agreement and a resulting consent decree with the NRDC and Sierra Club. This agreement committed DuPont to a six-year study of mercury in the South River ecosystem. Phase I of the study has been completed and has generated valuable information characterizing the extent of mercury contamination. Phase II will focus on specific sources of mercury and mercury methylation sites. Following the completion of the study, the parties will negotiate remedial options.

- Natural Resource Damage Assessment (NRDA) Process – The U.S. Fish and Wildlife Service has initiated a Natural Resource Damage Assessment (NRDA) on the South River. The NRDA program is designed to identify the natural resources injured by contamination, recover damages from responsible parties, and plan and carry out restoration activities. This process is currently in the damage assessment phase in the South River, but ultimately there is an expectation of restoration activities in the watershed.

- Resource Conservation and Recovery Act (RCRA) Clean up – Under USEPA oversight, DuPont is currently conducting a RCRA facility investigation at the former DuPont plant site. This activity has involved groundwater, stormwater, and soil testing on the plant site. Soon, corrective action measures will be taken to address solid waste management units that pose a human health or ecological risk.

- TMDLs for Other Pollutants – In addition to the mercury TMDL, TMDLs are also being developed for bacteria, sediment, and phosphorus in the South River. Implementation plans that specifically address these pollutants will also be required. In many cases, elements of these plans will also assist in reducing mercury inputs. For example, best management practices to reduce sediment loading in flood plain areas will also reduce the loading of mercury attached to those sediments. Exclusion of livestock from the river to reduce bacteria loading will also reduce trampling of the banks and channel margin sources of mercury.

### 5.4.3. Implementation Funding Sources

The implementation of pollutant reductions from nonpoint sources typically relies heavily on incentive-based programs. Therefore, the identification of funding sources for nonpoint source implementation activities is a key to success. Typical sources for implementation funding include the U.S. Department of Agriculture's Conservation Reserve Enhancement and Environmental Quality Incentive Programs, USEPA Section 319 funds, the Virginia State Revolving Loan Program (also available for permitted activities), Virginia Agricultural Best Management Practices Cost-Share Programs, the Virginia Water Quality Improvement Fund (available for both point and nonpoint source pollution), tax credits and landowner contributions. These traditional sources of funding may play a limited role in the implementation of the mercury TMDL. Their role will likely be in funding implementation of TMDLs for bacteria, sediment, and phosphorus in the South River, which will provide ancillary mercury reductions. Other state sources of funding, such as the Virginia Environmental Emergency Response Fund (VEERF), could also apply to mercury clean up in the South River.

Because the mercury impairment on the South River resulted from legacy contamination at the former DuPont site, DuPont retains some obligations with respect to funding clean up. These obligations include existing and potential settlement agreements, RCRA corrective actions, and NRDA restoration activities. While the details of remediation activities or funding levels have not yet been established within any of these programs, DuPont has committed to engaging in each process.

## 5.5. FOLLOW-UP MONITORING

Following the development of the TMDL, VADEQ will continue to monitor methylmercury levels in fish from the impaired rivers through the Fish Tissue and Sediment Monitoring Program. This program monitors the levels of organic and inorganic contaminants (including mercury) in fish and sediment across the Commonwealth. From year to year, routine monitoring rotates among the major river basins in Virginia.

In addition to routine fish and sediment monitoring, VADEQ has instituted a 100-yr monitoring program for mercury in the South River and South Fork Shenandoah River. As a result of a 1984 settlement agreement between DuPont and the SWCB, DuPont established a trust fund to implement this 100-yr monitoring effort. The monitoring schedule includes periodic monitoring of mercury in fish, sediment, water, and flood plain soils throughout 2092. Lastly, SRST members continue to conduct ongoing monitoring of mercury in the South River system, including water, sediment, soils, invertebrates, fish, reptiles, birds, and mammals. SRST members have suggested yearly monitoring of young-of-the-year fish in order to more dynamically track ongoing trends and progress during implementation. This suggestion has value and should be considered during Implementation Plan development.

VADEQ staff, in cooperation with VDH and the SRST, will continue to use data from the various monitoring programs to evaluate the accuracy of fish consumption advisories, reductions in pollutants (“water quality milestones” as established in the IP), the effectiveness of the TMDL in attaining and maintaining water quality standards, and the success of implementation efforts.

## 5.6. ATTAINABILITY OF DESIGNATED USES

In some streams for which TMDLs have been developed, factors may prevent the stream from attaining its designated use. In order for a stream to be assigned a new designated use, or a subcategory of a use, the current designated use must be removed. To remove a designated use, the state must demonstrate that the use is not an existing use, and that downstream uses are protected. Such uses will be attained by implementing effluent limits required under §301b and §306 of the Clean Water Act and by implementing cost-effective and reasonable best management practices for nonpoint source control (9 VAC 25-260-10 paragraph I).

The state must also demonstrate that attaining the designated use is not feasible because:

1. Naturally occurring pollutant concentration prevents the attainment of the use;

2. Natural, ephemeral, intermittent or low flow conditions prevent the attainment of the use unless these conditions may be compensated for by the discharge of sufficient volume of effluent discharges without violating state water conservation;

3. Human-caused conditions or sources of pollution prevent the attainment of the use and cannot be remedied or would cause more environmental damage to correct than to leave in place;

4. Dams, diversions or other types of hydrologic modifications preclude the attainment of the use, and it is not feasible to restore the waterbody to its original condition or to operate the modification in such a way that would result in the attainment of the use;

5. Physical conditions related to natural features of the water body, such as the lack of proper substrate, cover, flow, depth, pools, riffles, and the like, unrelated to water quality, preclude attainment of aquatic life use protection; or

6. Controls more stringent than those required by §301b and §306 of the Clean Water Act would result in substantial and widespread economic and social impact.

This and other information is collected through a special study called a Use Attainability Analysis (UAA). All site-specific criteria or designated use changes must be adopted by the SWCB as amendments to the water quality standards regulations. During the regulatory process, watershed stakeholders and other interested citizens, as well as the USEPA, will be able to provide comment during this process. Additional information can be obtained at http://www.deq.virginia.gov/wqs/.

The process to address potentially unattainable reductions based on the above is as follows: As a first step, measures targeted at the controllable, anthropogenic sources identified in the TMDL's staged implementation scenarios will be implemented. The expectation would be for the reductions of all controllable sources to the maximum extent practicable using the implementation approaches described above. VADEQ will continue to monitor biological health and water quality in the stream during and subsequent to the implementation of these measures to determine if water quality standards are attained. This effort will also help to evaluate if the modeling assumptions were correct. In the best-case scenario, water quality goals will be met and the stream's uses fully restored using effluent controls and BMPs. If, however, water quality standards are not being met, and no additional effluent controls and BMPs can be identified, a UAA would then be initiated with the goal of re-designating the stream for a more appropriate use or subcategory of a use.

A 2006 amendment to the Code of Virginia under 62.1-44.19:7E provides an opportunity for aggrieved parties in the TMDL process to present to the SWCB reasonable grounds indicating that the attainment of the designated use for a water is not feasible. The Board may then allow the aggrieved party to conduct a UAA according to the criteria listed above and a schedule established by the Board. The amendment further states that "If applicable, the schedule shall also address whether TMDL development or implementation for the water shall be delayed."

# 6. PUBLIC PARTICIPATION

Public participation was elicited at every stage of the TMDL development in order to receive input from stakeholders and to apprise the stakeholders of the progress made. Public participation was encouraged through holding public meetings in the watershed and by forming a Technical Advisory Committee (TAC). The TAC generally consisted of a subset of SRST members that provided input and assistance to VADEQ during the TMDL development. The goal of the TAC was to make sure that the technical aspects of the study (including model inputs and assumptions) were accurate as well as acceptable to the stakeholders.

On July 17, 2006, VADEQ held a public meeting at the Waynesboro Municipal Building to explain the South River mercury impairment to local citizens and describe the TMDL development process. The meeting was advertised through signs and posters throughout the watershed, e-mail announcements, letters to VPDES permit holders, notice publication in the Virginia Register, and press releases to the local media. Approximately 18 people attended the meeting. At the meeting, VADEQ explained the mercury impairment in the South River, described the TMDL process, and provided an open invitation to participate on the TAC. Handouts of the presentation were made available to attendees of the meeting and were distributed electronically upon request to those that were not able to attend the meeting.

The TAC met on seven occasions to discuss progress on the mercury TMDL. The TAC met once prior to the first public meeting on February 7, 2005, and then quarterly from October 2007 through January 2009. At each meeting, the TAC was updated on the status of the TMDL and asked to provide input on the model development. Prior to a final public meeting, the TAC was provided a preliminary draft of the TMDL report for comment and input.

On June 11, 2009, a second public meeting was held in the South River watershed. This meeting was once again advertised through e-mail announcements, notice publication in the Virginia Register, and through press releases to the local media. Approximately ? people attended this final public meeting. At the meeting, VADEQ presented the draft TMDL report to the public and explained its development and conclusions. An executive summary of the draft report was made available to the public at the meeting. The full report was made available on the VADEQ website at: https://www.deq.virginia.gov/TMDLDataSearch/DraftReports.jspx. Following the meeting, a 30-day public comment period on the draft was initiated. ? comments were received on the draft during the public comment period. VADEQ responded to all comments received and revised the draft report appropriately.

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# ATTACHMENT 1:

Eggleston, J. 2009. *Mercury Fluxes in the South River of the Shenandoah Valley of Virginia and Development of Mercury Total Maximum Daily Loads (TMDLs) for the South River, South Fork Shenandoah River, and Shenandoah River*. U.S. Geological Survey Scientific Investigations Report 2008-XXX, XXX p.

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# Mercury Loads in the South River and Simulation of Mercury Total Maximum Daily Loads (TMDLs) for the South River, South Fork Shenandoah River, and Shenandoah River: Shenandoah Valley, Virginia



Prepared in cooperation with the Virginia Department of Environmental Quality and the U.S. Environmental Protection Agency

Scientific Investigations Report 2009-XXX

**U.S. Department of the Interior**
**U.S. Geological Survey**

**Cover. South River. View looking downstream from the old Route 611 bridge near Dooms, Virginia, water-quality monitoring equipment in foreground.**
*(photograph by Jack Eggleston, U.S. Geological Survey, June 2005).*

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# Contents

## Figures

## Tables

River at Harriston, VA (U.S. Geological survey station no. 01627500), April 1, 2005, through March 31, 2005.

42. Calculated total maximum daily loads of mercury for listed waters in the Shenandoah Valley, Virginia.

## CONVERSION FACTORS and DATUM

| Multiply | By | To obtain |
|---|---|---|
| | **Length** | |
| inch (in.) | 2.54 | centimeter |
| foot (ft) | 0.3048 | meter |
| mile (mi) | 1.609 | kilometer |
| | **Area** | |
| acre | 4,047 | square meter |
| acre | 0.4047 | hectare |
| square mile ($mi^2$) | 259.0 | hectare |
| square mile ($mi^2$) | 2.590 | square kilometer |
| | **Volume** | |
| gallon (gal) | 3.785 | liter |
| gallon (gal) | 0.003785 | cubic meter |
| million gallons (Mgal) | 3,785 | cubic meter |
| cubic foot ($ft^3$) | 0.02832 | cubic meter |
| acre-foot (acre-ft) | 1,233 | cubic meter |
| | **Flow** | |
| cubic foot per second ($ft^3/s$) | 0.02832 | cubic meter per second |
| Million gallons per day (Mgal/d) | 0.04381 | cubic meter per second |
| inch per hour | 0.0254 | meter per hour |
| inch per year | 2.54 | centimeter per year |
| | **Mass** | |
| ounce, avoirdupois (oz) | 28.35 | gram (g) |
| pound, avoirdupois (lb) | 0.4536 | kilogram |
| pound per acre (lb/acre) | 1.121 | kilogram per hectare |

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD83). Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88). The term "water year" is defined as the 12-month period from October 1 for any given year through September 30 of the following year. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months. Thus, the year ending September 30, 1999, is called the "1999" water year.

## ABBREVIATIONS and ACRONYMS

| | | |
|---|---|---|
| CBM5 | - | Chesapeake Bay Watershed Model, Phase 5 |
| HRU | - | Hydrologic Response Unit |
| HSPEXP | - | Expert System for the Calibration of the Hydrological Simulation Program– FORTRAN |
| HSPF | - | Hydrological Simulation Program - FORTRAN |
| TMDL | - | Total Maximum Daily Load |
| USGS | - | U.S. Geological Survey |

# Mercury Loads in the South River of the Shenandoah Valley, Virginia and Development of Mercury Total Maximum Daily Loads (TMDLs) for the South River, South Fork Shenandoah River, and Shenandoah River

Jack Eggleston



## Abstract

Due to elevated levels of methylmercury in fish, three streams in the Shenandoah Valley of Virginia have been placed on the State's 303d list of contaminated waters. These streams, the South River, the South Fork Shenandoah River, and parts of the Shenandoah River, are downstream of the city of Waynesboro, where mercury waste was discharged from 1929-1950 at an industrial site. To evaluate mercury contamination in fish, this total maximum daily load (TMDL) study was performed in a cooperative effort between the U.S. Geological Survey, the Virginia Department of Environmental Quality, and the U.S. Environmental Protection Agency. The investigation focused on the South River watershed, a headwater of the South Fork Shenandoah River, and extrapolated findings to the other affected downstream rivers. A numerical model of the watershed, based on Hydrological Simulation Program- FORTRAN (HSPF) software, was developed to simulate flows of water, sediment, and total mercury. Results from the investigation and numerical model indicate that contaminated flood-plain soils along the riverbank are the largest source of mercury to the river. Mercury associated with sediment accounts for 96 percent of the annual downstream mercury load (181 of 189 kilograms per year) at the mouth of the South River. Atmospherically deposited mercury contributes a small load (less than 1 percent) as do point sources, including current discharge from the historic industrial source area. In order to determine how reductions of mercury loading to the stream

could reduce methylmercury concentrations in fish tissue below the U.S. Environmental Protection Agency criterion of 0.3 milligrams per kilogram, multiple scenarios were simulated. Bioaccumulation of mercury was expressed with a site-specific exponential relation between aqueous total mercury and methylmercury in smallmouth bass, the indicator fish species. Simulations indicate that if mercury loading were to decrease by 98.9 percent from 189 to 2 kilograms per year, fish tissue methylmercury concentrations would drop below 0.3 milligrams per kilogram. Based on the simulations, the estimated maximum load of total mercury that can enter the South River without causing fish tissue methylmercury concentrations to rise above 0.3 milligrams per kilogram is 2.03 kilograms per year for the South River, and 4.12 and 6.06 kilograms per year for the South Fork Shenandoah River and Shenandoah River, respectively.

## Introduction

Three rivers in the Shenandoah Valley of Virginia are contaminated with mercury and have been designated as "impaired" on Virginia's 303d list of contaminated waters due to fish consumption advisories issued by the Virginia Department of Health. These rivers, the South River, South Fork Shenandoah River, and the Shenandoah River between Front Royal and the confluence with Craig Run (fig. 1), are regulated by the Virginia Department of Environmental Quality (VDEQ) under the Total Daily Maximum Load (TMDL) Program, which develops plans to restore and maintain water quality for impaired waters.

This study by the U.S. Geological Survey (USGS), performed in cooperation with the U.S. Environmental Protection Agency (USEPA), VDEQ, and the South River Science Team, an interdisciplinary scientific group studying mercury in the South River, provides a scientific foundation for the VDEQ to establish mercury TMDLs for the three rivers. Results of this study will be used by VDEQ to develop an implementation plan to restore water quality in the three rivers so that fish tissue methylmercury concentrations are below 0.3 mg/kg (milligrams mercury per kilogram of fish tissue). The watershed modeling approach used to develop a mercury TMDL for the South River could be applied in other watersheds with comparable legacy mercury contamination.

**FIGURE 1 NEAR HERE**

## Background and History

Elevated levels of methylmercury in fish tissue have caused parts of the South River, the South Fork of the Shenandoah River, and the Shenandoah River to be placed on Virginia's 303(d) list of impaired waters and the Virginia Department of Health has restricted fish consumption from these rivers (fig. 1). The affected rivers are: 24.63 mi (miles) of the South River from the DuPont foot bridge in Waynesboro downstream to the headwaters of the South Fork Shenandoah River; the entire 100.96 mi of the South Fork Shenandoah River; 0.67 mi of the North Fork Shenandoah River from its mouth upstream to the Riverton Dam; and 29.83 mi of the Shenandoah River from the confluence of the North Fork and South Fork Shenandoah Rivers downstream to the confluence with Craig Run. Selected characteristics of the three rivers and the uncontaminated North River are listed in table 1.

Table 1. Selected characteristics of the North, South, South Fork Shenandoah, and Shenandoah Rivers, Virginia. [$mi^2$, square miles; Avg., average; R., river]

| Name of River | Drains to | Drainage area ($mi^2$) | On 303(d) list for mercury | Known industrial mercury sources |
|---|---|---|---|---|
| North | South Fork Shenandoah | 818 | No | No |
| South | South Fork Shenandoah | 235 | Yes | Yes |
| South Fork Shenandoah | Shenandoah | 1649 | Yes | Yes, from South R. |
| Shenandoah | Potomac | 2899 *(to Craig Run)* | Yes | Yes, from South R. |

A textile plant in Waynesboro is known to have discharged mercury to the South River from 1929 to 1950 (Bolgiano, 1980), when it was owned and operated by DuPont. Mercury released during that period has spread downstream, with the highest concentrations found within the 24 mi of the South River from the plant site downstream to its confluence with the South Fork Shenandoah River. DuPont has performed extensive site assessment and investigations at the plant site under the USEPA Resource Conservation and Recovery Program (DuPont Corporate Remediation Group, 2003a-b, and 2006a-b). The State of Virginia began regular monitoring of mercury in the late 1970s and is scheduled to continue monitoring through the year 2092. Other studies of mercury in the South River watershed are being conducted by members of the South River Science Team, a group of scientists and representatives from local universities, conservation groups, state and federal government agencies, DuPont, and its consultants. Data collected for these other studies provided an important foundation for this study.

Mercury concentrations remain elevated above background levels in soil and ground water at the plant site and some mercury still enters the river from the plant site through surface runoff, ground water, and permitted point-source discharges (DuPont Corporate Remediation Group, 2006a-b). Atmospheric mercury is deposited on the watershed by wet and dry deposition (U.S. Environmental Protection Agency, 2007). The largest current (2009) source of mercury to the river may be erosion of contaminated flood-plain and channel margin sediments, which have elevated mercury concentrations and were estimated to contain at least 57,000 lbs (pounds) of mercury along the South River alone (Bolgiano, 1980).

The present study was performed to quantify sources of mercury to the river and develop a simulation model that could be used to examine relations between mercury loading to the river and mercury concentrations in the water column. The model was then used to estimate mercury TMDLs for the listed rivers.

## Regulatory Approach and Total Maximum Daily Load Scope

When a water body is placed on the 303d list of contaminated waters, a regulatory requirement is triggered for a cleanup plan to be developed for the water body. The TMDL approach is based on the idea that if contaminant concentrations in a water body need to be below a specified maximum level, then only a limited amount of the contaminant can be allowed to enter the water body. A study is typically performed to determine a daily total maximum contaminant load (TMDL) so that contaminant concentrations remain below the maximum level. This study estimates the maximum daily loads of mercury to the South River, South Fork Shenandoah River, and Shenandoah River so that methylmercury concentrations in fish tissue can be kept below the USEPA ambient water-quality criterion of 0.3 mg methylmercury/kg fish (U.S. Environmental Protection Agency, 2001).

Fish tissue total mercury and methylmercury concentrations have been monitored in the South River, the South Fork Shenandoah River, and the Shenandoah River by the VDEQ since 1990. Methylmercury typically makes up about 90 percent of the total mercury present in South River fish (Virginia Department of Environmental Quality, 1999 and 2008a). Total mercury concentrations in smallmouth bass, the indicator fish, have been consistently elevated in the South River since 1990, averaging above 1.0 ppm (parts per million), and individual fish have had concentrations higher than 3.0 ppm. In the South Fork Shenandoah River and Shenandoah River, average methylmercury concentrations have been somewhat lower, but in 2007 were still above 0.3 mg/kg at all monitoring stations. Although mercury concentrations in the water column itself have not exceeded any regulatory standards set by the USEPA or the VDEQ, high concentrations of mercury have been observed in fish because mercury bioaccumulates as it moves up the food chain. How fish tissue methylmercury concentrations correlate with water column concentrations in the South River and how a site-specific bioaccumulation factor (BAF) is used in this study are described in the VDEQ companion report to this study (Virginia Department of Environmental Quality, 2008b).

The purpose of the present report is to describe the current understanding of mercury transport in the South River watershed and to provide estimates of the mercury loading reductions needed to protect human health from risks posed by consumption of fish from the river. The area of investigation focused on the South River because the original mercury source was located there and the South River has had the highest mercury concentrations in the Shenandoah River watershed. This focus permitted a spatially intensive data-collection effort. Results from the South River are extrapolated downstream to estimate loading reductions needed to meet methylmercury fish tissue targets for the South Fork Shenandoah and Shenandoah Rivers.



## Description of the Study Area

The 234.6 mi$^2$ (square mile) South River watershed in the Shenandoah Valley of Virginia comprises the study area (fig. 1). The downstream (northern) end of the study area is at the town of Port Republic, where the South River joins the South Fork Shenandoah River. The southern and southeastern boundaries of the watershed are defined by the Blue Ridge Mountains, whereas the northwestern boundary is a low rise of hills. Elevations range from 1,037 ft (feet) at the mouth of the South River to 3,848 ft at the peak of the Blue Ridge Mountains. Land use is primarily forested (58 percent) or agricultural (31 percent) with developed (8 percent) land accounting for most of the remainder (Chesapeake Bay Program, 2002). The largest population center in the study area is Waynesboro, with a 2000 census population of 19,520. The entire study area has an estimated 2000 population of 34,184 (U.S. Census, 2000). The South Fork Shenandoah River and Shenandoah Rivers are included in the TMDL part of the study.

Precipitation in the study area averaged 43.0 in/yr (inches/year) from October 2000 through March 2005, on the basis of precipitation data from the Waynesboro sewage treatment plant. Average evapotranspiration (ET) for the city of Waynesboro is 29.6 in/yr (inches per year), on the basis of spatially averaged data from multiple weather-monitoring stations outside the watershed from January 1984 through March 2007 (Chesapeake Bay Program, 2006). Annual streamflow at Harriston (01627500), the most downstream streamflow-gaging station in the study area, averaged 261.3 $ft^3/s$ (cubic feet per second) for the full period of record (fig. 2 and table 2). This flow is equivalent to 16.7 in/yr over the 212-$mi^2$ watershed above the Harriston gage.

**FIGURE 2 NEAR HERE**

Table 2. Streamflow-gaging stations and water-quality monitoring sites used in the study, South River, Virginia, 2005-2007. [USGS, U.S. Geological Survey; $mi^2$, square miles; "-" before a number indicates upstream; $ft^3/s$, cubic feet per second]

| USGS streamflow-gaging stations and water-quality monitoring sites | | | | |
|---|---|---|---|---|
| USGS station name<br>Station number | South River near Waynesboro<br>01626000 | South River near Dooms<br>01626850 | South River at Dooms<br>01626920 | South River at Harriston<br>01627500 |
| Location | Waynesboro | Hopeman Parkway | Dooms | Harriston |
| Streamflow monitoring (this study) | yes | yes | none | yes |
| Water-quality sampling (this study) | yes | none | yes | yes |
| Drainage area ($mi^2$) | 127 | 148 | 164 | 212 |
| River miles downstream from plant site | -2.8 | 2.3 | 5.3 | 16.5 |
| Streamflow record period | 1952-2008 | 1974-1997, 2005-2008 | none | 1926-1951, 1969-2008 |
| Mean annual flow ($ft^3/s$) | 150 | 214 | no data | 261 |

## Previous Studies

A history of mercury in the South River was obtained from studies and reports located in the VDEQ Office in Harrisonburg, Virginia. Since DuPont announced in the fall of 1977 that mercury had been found in the soil at its Waynesboro plant, numerous studies have documented mercury contamination at the plant site and in the downstream watershed (Paylor, 1977; Bolgiano, 1980; Todd, 1980; Old Dominion University, 1996, 1997, 1998; Messing and Winfield, 1998). Mercury sulphate was used by DuPont as a catalyst in fabric manufacturing from 1929 to 1950. Although the majority of the mercury catalyst was captured and reused, losses to the river resulted in widespread mercury contamination downstream (Bolgiano, 1980). Other potential sources of mercury in the watershed including agricultural fungicides, mercury in precipitation, and hydraulic seals in industrial equipment, have been documented, but appear insignificant relative to the large mass of mercury released from the plant site.

The Bolgiano study (1980) estimated that there were 57,000 lbs of mercury in the South River and the adjacent flood plain and a further 20,000 lbs in the South Fork Shenandoah River and the adjacent flood plain. A later study estimated 1,800 lbs of mercury in river sediments downstream of the plant site and 97,200 lbs of mercury in flood-plain soils (Lawler, Matusky, & Skelly Engineers, 1989).

Environmental concentrations of mercury in the South River have not changed appreciably since they were first measured in the late 1970s (Bolgiano, 1980; Old Dominion University 1996, 1997, 1998; Virginia Department of Environmental Quality, 1999, 2008a). Mercury concentrations in water, sediment, and biota vary with time and location, but do not show an obvious temporal trend, either positive or negative. Previous studies used different sampling and analytical methods, which makes comparison of results more difficult.

The development of low-concentration analytical methods for mercury in the 1980s that lowered detection limits by a factor of 1,000, from about 0.1 mg/L (milligrams per liter) to about 0.1 ng/L (nanograms per liter), has made it possible to detect aqueous mercury in the South River.

## Modeling Approach

This study used the numerical model Hydrologic Simulation Program- FORTRAN (HSPF) to simulate the transport of water, sediment, and mercury in the South River watershed. The model allows mass balance calculations of all three media and captures the transient fluctuations in flows and concentrations that occur in the watershed. After calibrating model parameters to match observed existing conditions, the model was then used to simulate hypothetical future conditions such as reductions in mercury loads to the river. The model can be modified in the future to incorporate new observations or additional processes that are found to affect mercury transport and fish tissue concentrations in the South River.

The choice of modeling software was guided by needed capabilities and potential regulatory acceptance. HSPF was chosen primarily because of its ability to simulate all media of interest in the South River watershed and stream system at the desired time scales. HSPF is also capable of simulating the transport of water, sediment, and mercury as well as phase exchange of mercury, all of which are important to mercury transport in the South River watershed. The time-series based simulations performed by HSPF allow for a 1-hour simulation period; this is fast enough to simulate changing river conditions during floods while still allowing long-term simulations that reflect average conditions. HSPF is also readily accepted by the regulatory community for TMDL purposes and many TMDL studies approved by the USEPA have used it.

The timeline for this study is presented in figure 3, along with the timeframes used for the modeling. Data collection in the South River watershed by the VDEQ and other groups has been ongoing since the 1970s. USGS streamflow monitoring has been ongoing since 1926, and data were collected specifically for this study from April 2005 through March 2007. The three components of the watershed model were calibrated and verified separately using the time periods shown in figure 3.

**FIGURE 3 NEAR HERE**

## Data Collected by the U.S. Geological Survey for This Study

Data were collected by USGS personnel over a 2-year (April 2005 through March 2007) field program. Goals of the field sampling and monitoring program were to collect data that would (1) characterize the locations and concentrations of mercury, (2) improve understanding of mercury loads in the watershed, and (3) allow calibration of a watershed mercury transport model. Most of the data were collected from three USGS monitoring stations along the South River near Waynesboro (01626000), at Dooms (01626920), and at Harriston (01627500) (fig. 2, table 2). Samples also were collected periodically from other sites along the river and at other locations such as pipe outfalls, ground-water wells, and riverbanks to guide model parameterization.

Data were also compiled from other organizations and from previous studies. These additional data help in understanding mercury in other media, such as fish and ground water, and provide an independent measure for checking model calibration.

## Streamflow

At three streamflow-gaging stations (01626000, 01626850, and 01627500) on the South River 15-minute and daily average streamflow values were collected using standard USGS methods (Rantz and others, 1982; Kennedy, 1983). The daily streamflow data are available online and at the USGS National Water Information System (NWIS) website http://waterdata.usgs.gov/nwis/. Streamflow data were used to calibrate the watershed model and, in combination with concentration values, used to calculate sediment and mercury loads.

The average of annual mean streamflow for the period of record increased from 150 $ft^3/s$ at Waynesboro 2.8 mi upstream of the plant to 261 $ft^3/s$ at Harriston 16.5 mi downstream of the plant site (table 2). Annual average flows varied widely, with a lowest measured annual average flow at Harriston of 70 $ft^3/s$ and highest of 516 $ft^3/s$ (fig. 4).

**FIGURE 4 NEAR HERE**

## Water Quality

At the beginning of the project, it was not clear which water-quality parameters would control or correlate with fish tissue methylmercury concentrations and therefore be important to study. Therefore data collection was designed to measure water-quality parameters that had been shown at other mercury contaminated sites to correlate with mercury transport and mercury concentrations in fish (Yin and Balogh, 2002; Gilmour and others, 1998). The following water-quality parameters were selected for monitoring in the South River: mercury (particulate and filtered concentrations of total mercury and methylmercury in various media), suspended sediment concentration, turbidity, dissolved organic carbon, chloride, sulfate, pH, and temperature. The last five parameters were selected with the specific intent of discovering correlations to methylmercury concentrations in water. Near the end of the data-collection program, it was decided that the study should focus only on total mercury because total mercury had the strongest correlation with fish tissue methylmercury concentrations in the South River. For this reason, only water-quality results for suspended sediment concentration, turbidity, and mercury concentrations are presented. The other parameters (dissolved organic carbon, chloride, sulfate, pH, and temperature) are not presented because they did not show a strong correlation with methylmercury concentrations.

## Methods

At each stream monitoring site, vertically integrated grab samples were collected from a single lateral location at the centroid of flow under base-flow conditions. All water-quality samples were taken as single vertically integrated grab samples. Continuous water-quality and grab sample data from this study can be accessed at the USGS NWIS website http://waterdata.usgs.gov/nwis/.

Surface-water samples were collected from bridges at the monitoring locations: Waynesboro (01626000), Dooms (01626920), and Harriston (01627500) (fig. 2). After each sampling event bottles were sent for analysis to the USGS Eastern Region Sediment Laboratory, the USGS National Water Quality Laboratory, and the USGS Mercury Laboratory (tables 3, 4).

Table 3. Water-quality sample treatments and laboratories used in the study. [mg/L, milligrams per liter; mL, milliliter; °C, degrees Celsius; USGS, U.S. Geological Survey]

| Analyte | Laboratory | Sample Container | Field Treatment | Detection Limit (mg/L) |
|---|---|---|---|---|
| Dissolved organic carbon | National Water-Quality Laboratory | 125-mL amber glass | Filter immediately, acidify with $H_2SO_4$ , and preserve at 4°C | 0.33 |
| Sulfate | | 250-mL plastic | Filter immediately and preserve at 4°C | 0.18 |
| Chloride | | | | 0.20 |
| Suspended sediment concentration | USGS Eastern Region Kentucky Sediment Lab | 1-pint glass | Preserve at 4°C | 1 |

A large percentage of mercury in the water column is typically bound to suspended particulate matter (Hem, 1989), so suspended sediment concentrations were measured in this study. Suspended sediment data were used to calibrate the numerical model for sediment transport as discussed in a later section, Sediment Model Calibration Results. Raw water samples were collected in 1-pint glass bottles and filtered with a 1.5-µm (micrometer) glass fiber filter during analysis of suspended sediment concentration (Guy, 1969). (Sampling and processing details are available online at http://ky.water.usgs.gov/technical_info/dist_sedlab_files/sed_lab.htm.)

Horizontal variability in water-quality constituent concentrations is not reflected in a single vertically integrated sample, unlike a full representative cross-sectional sample. The decision to collect single vertically integrated samples was made to decrease the possibility of contaminating trace-level mercury concentrations due to the extra handling and equipment involved. A full concurrent cross-sectional sampling event was performed at the Harriston station in August 2005 under base-flow conditions to test the representativeness of a single vertically integrated sample. The results indicated no consistent patterns of horizontal variation in the water-quality parameters tested (THG, $THG_F$, $THG_P$, $THG_{SS}$, MHG, chloride, sulfate, pH, suspended sediment, and specific conductivity). Data from other studies have shown higher filtered mercury ($THG_F$) concentrations in the South River closer to riverbanks and to sediment-water interfaces (Turner and Jensen, 2007) under base-flow conditions, however.

Continuous monitoring of in-stream water quality was performed by hanging probes from bridges into the river near Waynesboro, at Dooms, and at Harriston (table 2). Probes were located close to the centroid of flow at deep points in the river so that they would remain submerged under low water conditions. Continuous water-quality data for the three South River monitoring stations are available on the USGS NWIS website at http://waterdata.usgs.gov/nwis/. Probes were calibrated and serviced on a monthly basis. The continuous parameters were collected using a YSI multi-parameter field meter (model 6920 or similar) following standard USGS protocol (Wagner and others, 2000).

Water-quality samples analyzed for mercury were collected according to established sampling protocol for ultra-trace metals; aqueous and sediment samples were collected using the "clean hands – dirty hands" technique (Horowitz, 1991; Horowitz and others, 1994; U.S. Environmental Protection Agency, 1996; Ward and Harr, 1990). Surface-water samples were collected in 2-L (liter) Teflon bottles precleaned by the USGS Mercury Laboratory. The precleaned 2-L Teflon bottles were placed into a stainless steel bottle holder, and then lowered into the river from a bridge. A single vertically integrated sample was collected at each monitoring site and capped, placed on ice, and shipped to arrive at the USGS Mercury Laboratory within 24 hours. Laboratory personnel then processed the sample using techniques based on USEPA Method 1631 (Olson and DeWild, 1999; DeWild and others, 2002; U.S. Environmental Protection Agency, 2002; Olund and others, 2004). Filtering of mercury samples through a 0.7-µm filter was performed in the laboratory by USGS Mercury Laboratory personnel; no filtering of mercury samples was performed in the field. Detection limits for laboratory analyses of mercury are shown in table 4.

Table 4. Detection limits for mercury analyses. [USGSML = U.S. Geological Survey Mercury Laboratory; mL, milliliters; ng/L, nanograms per liter; μg/g, micrograms per gram; °C, degrees Celsius; see table 6 for description of analyte abbreviations]

| Analyte | Laboratory | Sample Container | Field Treatment | Detection Limit | Units |
|---|---|---|---|---|---|
| Total filterable mercury ($THG_F$), Aqueous methylmercury (MHG) | USGS Mercury Laboratory | Precleaned Teflon from USGSML (250, 500, 1000, and 2000 mL) | Preserve at 4°C | 0.04 | ng/L |
| $THG_P$ | | | | 0.06 | ng/L |
| $THG_{SED}$ | | | | 0.30 | μg/g |

During a base-flow period in June 2006, pore-water samples were collected from the riverbank along the river's edge at one location upstream of the plant site at Waynesboro (01626000), and at three locations downstream of the plant site: Basic Park, 0.2 mi upstream of monitoring station 0162850; Steeles Run confluence, 0.4 mi upstream of monitoring station 01626850; and at Dooms (01626920). Pore-water samples were collected using a Teflon drivepoint connected to Teflon tubing driven by a peristaltic pump. Samples were drawn from depths of 5 and 15 cm (centimeters) below land surface into precleaned Teflon bottles and shipped to the USGS Mercury Laboratory for analysis as previously described. Sediment samples were collected from the same 5- and 15-cm depths using precleaned stainless steel implements, placed into precleaned Teflon bottles, and shipped on ice to the USGS Mercury Laboratory.

## Suspended Sediment

Results from the USGS suspended sediment concentration data collected for this study are summarized in table 5. Suspended sediment concentration was strongly affected by streamflow, generally increasing with increasing flows (fig. 5). Although the raw data show that Waynesboro had higher suspended sediment concentration values than Dooms and Harriston, this result is biased due to a greater proportion of stormflow samples collected at Waynesboro. When flow-corrected mean suspended sediment concentrations are calculated, Waynesboro exhibited a lower mean suspended sediment concentration than Dooms (table 5). Flow correction is performed by taking a weighted average that accounts for the magnitude of flow, assessed by streamflow duration at the time of sampling, and removes bias towards either low-flow or stormflow sampling. Results from the Harriston site show slightly lower mean and flow-weighted mean suspended sediment concentration values than the values from either the Waynesboro or Dooms sites.



Table 5. Suspended sediment concentrations and turbidity values, South River, Virginia, April 2005 through March 2007. [USGS samples only; FNU, Formazin nephelometric units; SSC, suspended sediment concentration; mg/L, milligrams per liter; %, percent].

| Statistic | | Monitoring Site Waynesboro (01626000) | Dooms (01626920) | Harriston (01627500) |
|---|---|---|---|---|
| Suspended Sediment Concentration (mg/L) | Count | 29 | 28 | 36 |
| | Mean | 56.4 | 39.4 | 38.2 |
| | Median | 8.0 | 6.5 | 7.5 |
| | Standard Deviation | 112.0 | 99.7 | 83.9 |
| | Range | 1-434 | 1-433 | 1-377 |
| Flow Weighted SSC* (mg/L) | Mean | 37.2 | 38.7 | 26 |
| Turbidity (FTU) | Period | 5/1/2005 to 4/1/07 | 4/21/2005 to 4/1/2007 | 6/3/2005 to 4/1/2007 |
| | Count | 62,588 | 63,052 | 58,595 |
| | % Data Coverage | 93% | 93% | 92% |
| | Mean | 9.1 | 8.2 | 7.1 |
| | Std. Deviation | 39.9 | 32.1 | 38.1 |

* *Corrected for flow bias as described in the Mercury/Surface Water section*

**FIGURE 5 NEAR HERE**

## Turbidity

Turbidity indicates the ability of a fluid to transmit light without scattering or absorption (Gray and Glysson, 2003). Turbidity was measured using the multiparameter probes and is reported in formazin nephelometric units (FNU) (fig. 6). Turbidity is used to develop a suspended sediment concentration time series. Turbidity results for the three monitoring stations in the study are summarized in table 5. Mean turbidity decreased from Waynesboro downstream to Harriston. Turbidity data collection from each probe was periodically interrupted due to conditions such as high water velocity and algae growth. During high flow events, interruptions in turbidity data were common and, because turbidity typically rose during storms by one to two orders of magnitude, the statistics in table 5 are almost certainly affected by the missing data.

**FIGURE 6 NEAR HERE**

## Mercury

Data were collected during this study to describe mercury concentrations in the South River, in piped discharges to the river, in ground water, and in soils. Collection of mercury data was made using standard USGS sample-collection techniques and followed a quality assurance plan to ensure that data were comparable, complete, and representative. Mercury analyses were performed by the USGS Mercury Laboratory in Middleton, Wisconsin.

## Units and Terms

Mercury concentrations are expressed in per mass or per volume units that depend on the medium being considered. The various mercury concentration units used in this report are defined in table 6.

Table 6. Description of units for mercury concentrations used in this report [ng/L, nanograms per liter; µg/g, micrograms per gram].

| Acronym | Description of concentration | Units |
|---|---|---|
| THG | Aqueous total mercury, typically calculated as the sum of $THG_F$ and $THG_P$. | Nanograms total Hg per liter of water (ng/L). |
| $THG_F$ | Aqueous filterable total mercury. | Nanograms total Hg passing a 0.7-µm filter per liter of water (ng/L). |
| $THG_P$ | Aqueous total mercury associated with non-filterable particulates. | Nanograms total Hg not passing a 0.7-µm filter per liter of water (ng/L). |
| $THG_{SS}$ | Total mercury on solids suspended in water, calculated as $THG_P$/suspended sediment concentration. | Micrograms total Hg per gram of dry suspended solids (µg/g). |
| $THG_{Sed}$ | Total mercury on soils or surface sediment. | Micrograms total Hg per gram of dry soil (µg/g). |
| MHG | Aqueous methylmercury. | Nanograms MeHg per liter of water (ng/L). |

## Surface Water

Mercury concentrations for the monitoring stations on the South River are shown in tables 7 and 8. Downstream of the plant site, mean THG concentrations were more than 70 times higher than at the Waynesboro monitoring station. Concentrations of mercury on suspended sediment ($THG_{SS}$) increased by a factor of more than 100 downstream of the plant site.

During most sampling events, the majority of mercury in the water column was associated with suspended particulate matter (Meybeck and Helmer, 1989). At the background reference station (Waynesboro) about 78 percent of aqueous mercury was particulate-bound, whereas downstream of the plant site, 98 percent and 96 percent of the mercury was particulate-bound, at Dooms and Harriston, respectively.

Table 7. Aqueous total mercury concentrations for the South River, April 1, 2005, through March 31, 2007. [USGS samples only; $THG_F$ , filterable total mercury; $THG_P$, particulate total mercury; THG, unfiltered mercury; ng/L, nanograms per liter; n, sample size]

| | | Aqueous Total Mercury | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $THG_F$ (ng/L) | | | $THG_P$ (ng/L) | | | $THG = THG_F + THG_P$ | | |
| Station ID | n | Mean | Median | Range | Mean | Median | Range | Mean | Median | Range |
| Waynesboro (01626000) | 30 | 1.0 | 0.4 | 0.1-3.7 | 3.3 | 0.8 | 0.3-19.8 | 4.3 | 1.3 | 0.5-23.5 |
| Dooms (01626920) | 28 | 7.4 | 7.2 | 2.7-14.5 | 291.9 | 100.3 | 14-2,730 | 299.3 | 103.6 | 17-2,740 |
| Harriston (01627500) | 36 | 13.6 | 12.9 | 4.0-33.2 | 319.2 | 99.6 | 13-4,020 | 332.8 | 115.0 | 18-4,042 |

Table 8. Concentrations of total mercury on suspended sediment in the South River, April 1, 2005, through March 31, 2007. [USGS samples only; $THG_{SS}$, mercury on suspended sediment; μg/g, micrograms per gram; n, sample size]

| | | Mercury on Suspended Sediment | | |
|---|---|---|---|---|
| | | $THG_{SS}$ μg/g | | |
| Station ID | n | Mean | Median | Range |
| Waynesboro (01626000) | 30 | 0.1 | 0.1 | 0.0-0.7 |
| Dooms (01626920) | 28 | 17.4 | 13.1 | 2-66 |
| Harriston (01627500) | 36 | 13.5 | 10.8 | 2-48 |

Total mercury (THG) concentrations increased with increasing streamflow (fig. 7). Filterable mercury $THG_F$ concentrations in nanograms per liter showed a slight positive correlation with streamflow (fig. 8), particularly at the Waynesboro reference station. The increase of filterable mercury concentrations with streamflow may be due to desorption of mercury from contaminated sediment entering the stream and(or) from higher inflows of precipitation and interflow, both of which have average $THG_F$ concentrations above 1.0 ng/L, or possibly from an increase in the concentration of colloidal particles passing the laboratory filter. $THG_p$ concentrations, the aqueous concentration of mercury associated with suspended particulates, showed a strong positive correlation with streamflow at all monitoring stations (fig. 9). $THG_{SS}$ concentration, the concentration of mercury on suspended particulates, showed a slight negative correlation with streamflow, (fig. 10). Therefore, it can be concluded that the large increase in THG seen during high flows was driven by the large increase in suspended sediment concentration (fig. 5).

**FIGURE 7 NEAR HERE**

**FIGURE 8 NEAR HERE**

**FIGURE 9 NEAR HERE**

**FIGURE 10 NEAR HERE**

The concentrations of mercury and suspended sediment based on sample data from the South River are listed in table 9. Mercury concentrations for other rivers, the North River near Burketown (01622000), an uncontaminated tributary to the South Fork Shenandoah River and the South Fork Shenandoah River near Luray (01629500), located 69 mi downstream of the mouth of the South River are listed in table 10. Concentrations listed in tables 9 and 10 are flow-weighted to remove sampling bias towards either stormflow or base-flow periods. Concentration values were grouped into 10 bins according to streamflow magnitude at time of sampling, defined by flow duration deciles of 0-10 percent, 10-20 percent, 20-30 percent, and so forth.  To calculate the mean concentrations shown in tables 9-10, mean concentrations were calculated for each decile and then these 10 decile mean concentrations were averaged.

Table 9.  Observed flow-weighted average sediment and mercury concentrations in the South River, Virginia, April 1, 2005, through March 31, 2007.  [USGS samples only; $ft^3/s$, cubic feet per second; ng/L, nanograms per liter; mg/L, milligrams per liter]

| USGS Monitoring Station | Observed Avg. Daily Streamflow ($ft^3/s$) | Flow-Weighted Average Concentration: Suspended Sediment (mg/L) | Flow-Weighted Average Concentration: THG (ng/L) |
|---|---|---|---|
| Waynesboro (01626000) | 167 | 37.2 | 3.2 |
| Dooms (01626920) | 225 | 38.7 | 336 |
| Harriston (01627500) | 276 | 26.0 | 237 |

Table 10.  Observed flow-weighted average mercury concentrations in rivers neighboring the South River, Virginia, January 2002 through March 2006.  [VDEQ samples only; $ft^3/s$, cubic feet per second; ng/L, nanograms per liter; n, sample size]

| US Geological Survey monitoring station ID | Drains to | Type | Average Daily Streamflow ($ft^3/s$) | Total Mercury Concentration: n | Total Mercury Concentration: (ng/L) |
|---|---|---|---|---|---|
| North River near Burketown, VA (01622000) | South Fork Shenandoah River | Reference site | 387 | 25 | 1.9 |
| South Fork Shenandoah near Luray, VA (01629500) | Shenandoah River | Mercury contaminated site | 1,422 | 25 | 10.8 |

Of the surface-water samples collected from the South River, 17 percent were either field blanks or replicate samples used for quality control and assurance.  Of the 22 $THG_F$ and $THG_P$ analytical values from the field blank samples, one was above 0.2 ng/L and was determined to be a laboratory clerical error and was dropped from the dataset.  Of the 26 $THG_F$ and $THG_P$ analytical values from replicate samples, the average paired concentration difference was 0.8 ng/L with no sampling biases found and the data were determined to be comparable and reproducible.

## Ground Water

In June 2006, pore-water samples were collected at multiple locations at the edge of the South River and analyzed for $THG_F$ concentrations. Results are shown in table 11. Pore-water $THG_F$ concentrations were higher than those found in either ground water from a contaminated flood plain (described later) or from the South River. Sediment collected during the same sampling events at these locations had high levels of mercury, and presumably, mercury in the soil is the source of the high dissolved mercury concentrations. No beads of elemental mercury were observed at the sampling locations.

Table 11. Concentrations of filterable total mercury $THG_F$ in riverbank pore water, South River, Virginia, June 2006. [USGS samples only; BLS, below land surface; mi, miles; n, sample size]

| | Filterable total mercury concentration (nanograms mercury per liter of water) | | | |
|---|---|---|---|---|
| | Waynesboro | Steeles Run | Basic Park | Dooms |
| Depth of Sample | (01626000) | 0.4 mi upstream of station 01626850 | 0.2 mi upstream of station 01626850 | (01626920) |
| 5 cm BLS | - | 158.0 (n=2) | 35.6 (n=2) | 164.0 (n=1) |
| 15 cm BLS | 1.4 (n=1) | 326.5 (n=2) | 217.7 (n=2) | - |

## Sediment

Sediment samples were collected from the river's edge during the June 2006 pore-water sampling event. These concentrations, shown in table 12, are similar to concentrations seen on suspended sediment in the South river (fig. 10) and to mean $THG_{Sed}$ concentration values for flood-plain and riverbank soils compiled from the South River Science Team database, described in a later section, Mercury in Soil.

Table 12. Concentrations of total mercury in riverbank sediment, South River, Virginia, June 2006. [USGS samples only; BLS, below land surface; cm, centimeters; mi, miles; n, sample size; nd, no data]

| | Total mercury concentration on sediment (micrograms mercury per gram dry sediment) | | | |
|---|---|---|---|---|
| | Waynesboro | Steeles Run | Basic Park | Dooms |
| Depth of Sample | (01626000) | 0.4 mi upstream of station 0162850 | 0.2 mi upstream of station 0162850 | (0162920) |
| 5 cm BLS | nd | 11.2 (n=2) | 4.2 (n=2) | nd |
| 15 cm BLS | nd | 11.3 (n=2) | 3.4 (n=2) | nd |

## Mercury Sorption to Suspended Solids

Mercury (THG) in the South River partitions between sorbed and dissolved phases. The data in tables 7 and 8 indicate a distribution coefficient (Kd) for total mercury in the South River of about 1,000,000 L/kg (liters/kilogram), or a log Kd of about 6, assuming that sorption was at equilibrium in the samples at the time of analysis. This Kd value of about 6 is seen both in the ratio of sampled mean $THG_F$ and $THG_{SS}$ concentrations (tables 7 and 8) and in laboratory batch tests by Mason (2006). A lot of spatial and temporal variation is present in this distribution coefficient, however, some of which corresponds to the location relative to the plant site. Average log Kd was lowest (5.1) upstream of the former DuPont plant site at the Waynesboro monitoring station (01626000), highest (log $K_d$ = 6.4) downstream at the Dooms monitoring station (01626920), and lower again (log Kd = 6.0) further downstream at the Harriston monitoring station (01627500). Partitioning ratios also correlated negatively with streamflow. Log Kd values, determined from the ratio of sampled $THG_F$ and $THG_{SS}$ concentrations, were higher during low flow than high flow at all three monitoring stations. At monitoring station 01626920, for example, mean log Kd was 6.25 for base-flow samples and 5.80 for stormflow samples. This variation may be due to various causes; non-equilibrium sorption (time delay to reach equilibrium) in combination with loads having varying proportions of dissolved and sorbed mercury, runoff sediment characteristics varying with river location, different mixing in the water column according to river location, chemical variations such as pH along the river, or other possible variables whose effects on mercury partitioning are currently not well understood for the South River. A constant and uniform log Kd value of 1,000,000 was used in the mercury transport model.

# Data Compiled From Other Sources

The South River is the subject of many past and ongoing studies, which provided valuable supplemental data to this study. Selection of data from other sources to include in this study was prioritized according to need, reliability, and public availability. Many other datasets not used or mentioned in this study are available from the VDEQ in Harrisonburg, Virginia or by request from the South River Science Team website (http://www.southriverscienceteam.org)

## Suspended Sediment

Suspended sediment data previously collected by the VDEQ were compiled. The VDEQ data were reported in units of milligrams per liter and, like USGS suspended sediment samples, are filtered with a 1.5-μm filter. But they were reported as "total suspended sediment" rather than "suspended sediment concentration," because of differences in laboratory methods, such as a sample split rather than a whole sample being analyzed. An additional difference between USGS and VDEQ suspended sediment data is that concentrations below detection limits were generally reported as 3 mg/L. This 3 mg/L value for VDEQ data was maintained for analysis in this study. The USGS suspended sediment concentration data had a reporting limit of 1.0 mg/L and reporting limit values were maintained at 1.0 for data analysis. In later sections of this report, the VDEQ total suspended sediment data and the USGS suspended sediment concentration data are treated as equivalent for purposes of discussion and illustration.

## Mercury in Surface Water

Mercury concentrations in surface water measured by the VDEQ were compiled to provide representation of time periods before April 2005, and coverage of rivers other than the South River. The VDEQ has had an extensive sampling program for mercury in the Shenandoah River watershed in place since the 1980s. Mercury concentration values used in this report were drawn from the VDEQ's database in August 2008. These data were not used in calibrating the watershed model, but provided an independent basis for checking model results. These data were also used to estimate mercury loads in the South Fork Shenandoah and Shenandoah Rivers.

Mercury concentrations in runoff and wastewater discharge from the plant site are measured by DuPont. These mercury data were made available to this study by DuPont, DuPont's contractors, and the USEPA.

## Atmospheric Mercury Deposition

Mercury is deposited from the atmosphere in both wet and dry forms. Data describing atmospheric mercury deposition were obtained from the USEPA Mercury Deposition Network (MDN) website (http://nadp.sws.uiuc.edu/mdn/). Two MDN sites are about 50 mi northeast of Waynesboro: Big Meadows (VA28), located on top of the Blue Ridge Mountains at an elevation of 3,524 ft, and Culpeper (VA08), located east of the Blue Ridge Mountains at an elevation of 535 ft, (fig. 11). Annual mercury wet deposition at both stations was 13.2 $\mu g/m^2$ during 2003. Actual mercury deposition rates in the study area may differ from this value. There is at least one coal-fired electric generation plant in the watershed (at the Invista/DuPont plant site), which has the potential to locally elevate mercury deposition rates. Dry deposition of mercury (the transfer of mercury from the atmosphere to the ground in the absence of precipitation), likely occurs, but no reliable data are available describing rates near the study area. A 1997 modeling study by the USEPA (U.S. Environmental Protection Agency, 1997, table 3-3), found that wet deposition accounts for 51 percent of total atmospheric mercury deposition in the continental U.S. whereas dry deposition accounts for 49 percent. Data shown in figures from the 1997 U.S. Environmental Protection Agency report indicate that most of the State of Virginia, including the South River study area, has a total Hg dry deposition rate ranging from 3 to 10 $ug/m^2$.

On the basis of the MDN numbers and the 1997 USEPA study, it is assumed that total atmospheric mercury deposition in the study area was 20.0 $\mu g/m^2/yr$ for the simulation period. Multiplying this value by 234 $mi^2$ ($6.1x10^8 m^2$) results in estimated atmospheric mercury input to the study area of 12.1 kg/yr. The modeling efforts described later use average atmospheric mercury concentrations that assume all mercury deposition takes place in the wet form. To calculate an average $THG_F$ concentration in precipitation, the total deposition of 20.0 $\mu g/m^2/yr$ was multiplied by average annual precipitation of 1.02 m/yr and by a unit correction factor to yield an average $THG_F$ concentration in precipitation of 21.79 ng/L.

Most of the atmospheric mercury deposited on the South River watershed binds to surface soils and does not reach the South River, as has been found in other watersheds (U.S. Environmental Protection Agency, 1997, vol. 3). This is evident from a mercury mass balance at the upstream Waynesboro river monitoring site. Using the same decile-weighting procedures that were used for the values in Table 9 yields an estimated mercury load for the South River at the Waynesboro monitoring station of 0.7 kg/yr. The estimated annual mass of mercury deposited from the atmosphere to the watershed above the Waynesboro monitoring station is 6.6 kg/yr, estimated by multiplying the deposition rate (20.0 ug/$m^2$) by the Waynesboro watershed area (127 $mi^2$). Comparing the two loads, only 11 percent of the estimated atmospheric mercury deposition upstream of the Waynesboro monitoring station reaches the South River.

**FIGURE 11 NEAR HERE**

## Mercury in Fish Tissue

Virginia State Agencies have collected fish from the South River for mercury analysis since the late 1970s. The Virginia Department of Health has placed fish consumption bans or advisories on the South River and the South Fork Shenandoah River since 1977 (Bolgiano, 1980). The VDEQ currently collects fish for mercury analysis, and the findings are summarized in their reports (Virginia Department of Environmental Quality, 1999, 2000, 2008a). Fish tissue mercury concentrations have not changed appreciably since monitoring started (Virginia Department of Environmental Quality, 2001). Fish tissue mercury concentrations along the South River from smallmouth bass collected and analyzed by the VDEQ from 1999 through 2007 are shown in figure 12. Upstream of the plant site, concentrations were generally below the USEPA 0.3 mg/kg criterion. Downstream from the plant site, fish tissue methylmercury concentrations rose rapidly for about 5 mi, and showed the highest concentrations between 5 and 12 mi downstream from the plant site.

Compared to fish tissue methylmercury concentrations from 20 other regions in the U.S. (Brumbaugh and others, 2001), the South River had higher fish tissue methylmercury concentrations than all water bodies except one, the Nahontan Reservoir in Nevada, which has been contaminated as a result of mercury mining. Unlike the sites studied by Brumbaugh and others (2001), the South River exhibits a strong correlation between fish Hg concentrations and aqueous THG concentrations. This strong correlation is discussed in the Virginia Department of Environmental Quality TMDL report accompanying this study (Virginia Department of Environmental Quality, 2008b). In the nearby North River watershed, where there is no known industrial mercury contamination, fish tissue methylmercury concentrations averaged 0.2 mg/kg in 2007 (Virginia Department of Environmental Quality, 2008a).

**FIGURE 12 NEAR HERE**

## Mercury in Soil

Additional data describing mercury concentrations in soils were compiled for use as input to the model. The $THG_{Sed}$ values in table 13 were derived from a database of field sample results collected by South River Science Team members and maintained by DuPont (http://www.southriverscienceteam.org) (DuPont, 2008). The mercury concentrations were measured in soils collected from depths of 0 to 1.0 m below land surface, and from a variety of settings including the river channel, riverbanks, and agricultural and forested flood plains. Values were grouped according to location along the river and mean values were calculated. In the model, these values are multiplied by loading coefficients that control the amount of mercury entering each model river reach from each hydrologic response unit representing contaminated flood-plain areas. During calibration, the loading coefficients were adjusted to match simulated THG values in the river reaches to observed values.

Table 13. Average concentrations of mercury in soil, South River watershed, Virginia, April 2003 through October 2006. [Samples from multiple sources compiled in the South River Science Team database. Mi, mile; HG, mercury; $THG_{Sed}$, mercury concentration on sediment or soil; µg/g, micrograms per gram; negative values indicate upstream of plant site]

| | Mi from Plant Site | | Soil HG Samples | | Model $THG_{Sed}$ value µg/g |
|---|---|---|---|---|---|
| Reach | From | To | Count | Average $THG_{Sed}$ µg/g | Final Calibrated Value |
| 1 | -30.0 | -2.5 | 2 | 0.01 | 0.07 |
| 2 (upstream) | -2.5 | 0 | 24 | 0.27 | 0.07 |
| 2 (downstream) | 0 | 2.3 | 145 | 13.9 | 13.9 |
| 3 | 2.3 | 5.3 | 137 | 16.2 | 16.7 |
| 4 | 5.3 | 16.5 | 245 | 17.2 | 16.7 |
| 5 | 16.5 | 24.0 | 41 | 7.6 | 7.6 |

## Mercury in Ground Water

Ground-water samples were collected in October 2006, from a pastured flood plain 1 mile upstream from the Dooms station (01626920) in a joint effort by the U.S. Environmental Protection Agency, the Virginia Department of Environmental Quality, and the U.S. Geological Survey. The flood plain is downstream of the plant site and known to have mercury contamination in surface soils. Ground-water samples were pumped from 18 wells that had been installed to depths within 30 ft of land surface. The samples analyzed for total mercury were collected and analyzed by the VDEQ following USEPA methods

1669 and 1631, Rev, E (U.S. Environmental Protection Agency, 1996, 2002), which have $THG_F$ detection limits of 1.5 ng/L.

Thirteen of the 18 samples had $THG_F$ concentrations below the detection limit of 1.5 ng/L. The maximum THGF concentration was 25.8 ng/L. When the non-detect values are set to zero, the mean $THG_F$ value of the 18 samples was 2.9 ng/L, which was later used as an input to the numerical watershed model.

## Development of Time-Series Data

The complex hydrologic conditions within the South River watershed are constantly changing, sometimes rapidly, when the river rises in response to a storm, for example. Time-series data describing these changing hydrologic conditions are needed to run the numerical watershed model and to calibrate the model. Time series were developed containing values for each required model input variable in regular intervals, typically 1 hour, to match the time step of the HSPF watershed model. These time-series data and their sources are summarized in table 14.

Table 14. Sources of time-series data used in the South River watershed model. [CBM5, Chesapeake Bay Community Watershed Model, Phase 5, (Chesapeake Bay Program, 2006); NOAA, National Oceanic and Atmospheric Administration; VDEQ, Virginia Department of Environmental Quality; VPDES, Virginia Pollutant Discharge Elimination System; USGS, U.S. Geological Survey]

| Time Series | Source of Data |
|---|---|
| Streamflow | Stage monitoring, USGS |
| Meteorology: rainfall, snowfall | CBM5 datasets, NOAA weather station data, and data supplied by Invista and the City of Waynesboro |
| Climatic conditions: air temp., wind speed, cloud cover, dew point, evapotranspiration, solar radiation | CBM5 datasets, NOAA weather station data |
| Suspended sediment concentration | Sample analyses and multiple linear regression, USGS and VDEQ datasets |
| Mercury concentrations | Sample analyses, VDEQ and USGS datasets |
| Point-source discharges | VPDES data, permittee records |

## Streamflow Time Series

Observed streamflow data were used to calibrate the hydrologic part of the numerical watershed model and to calculate regressed suspended sediment concentration values. Daily mean streamflow time series for the period October 1, 1990, through September 30, 2007, were developed for streamflow-gaging stations 01626000, 01626850, and 01627500 for calibration and verification of the hydrologic model. Hourly streamflow values for the same period were used to estimate suspended sediment concentration values as described in the next section(s). Both hourly and daily streamflow data were drawn from USGS-NWIS databases.

## Suspended Sediment Concentration Time Series

A time series of suspended sediment concentration was needed to calibrate the sediment part of the numerical watershed model. Time series allow more detailed and accurate model calibration than periodic grab sample values alone. Hourly time series of suspended sediment concentration at the primary monitoring stations (01626000, 01626920, and 01627500) were developed to match the hourly time step of the watershed model for the periods October 1, 1990, through September 30, 2000, and April 1, 2005, through March 31, 2007.

Suspended sediment concentration values were regressed using linear multiple regression models with independent variables of turbidity and various transformations of streamflow. Use of turbidity and transformed streamflow as independent parameters generally improves predictions of suspended sediment concentration by linear regression models, as has been demonstrated in other investigations (Rasmussen and others, 2005; Jastram, 2007). Suspended sediment concentration data available for the regression are from analyses of 78 grab samples (USGS only) collected at the three South River water-quality monitoring stations. The samples were collected during both base-flow and stormflow conditions at all three stations, as described earlier.

A suitable regression model had to be formulated from the many possible explanatory (independent) variables. At the start of the regression analysis, a suite of variables was tested for correlation with suspended sediment concentration. The following variables were then retained as possible explanatory variables in the linear regression model:

$Q$ = Streamflow ($ft^3/s$) measured concurrently with water sampling;
$log_{10}Q$ = Log of $Q$;
$Q^{½}$ = Square root of $Q$;
$Q_{slope}$ = Percent change in $Q$ from 1 hour previous;
$Q_{increase}$ = Absolute value change in $Q$ ($ft^3/s$) from 1 hour previous, (no negatives);
$Q_A$ = $Q$ normalized by watershed area; and
$Turb$ = Turbidity (FNU).

Of the several streamflow parameters, $Q_A$ exhibited the highest correlation with suspended sediment concentration ($R^2$ = 0.744). $Q_A$ was therefore retained in the regression model whereas $Q$, $log_{10}Q$, and $Q^{½}$ were excluded from the model because though they each have predictive value on their own, they correlate too strongly with $Q_A$ to be included in the multiple regression model. $Q_{increase}$ and $Q_{slope}$ were then redefined as follows:

$Q_{slope}$ = Percent change in $Q_A$ from 1 hour previous; and
$Q_{increase}$ = Change in $Q_A$ ($ft^3/s$) from 1 hour previous, negative values = 0.

The remaining four independent variables ($Q_{slope}$, $Q_A$, $Q_{increase}$, and *Turb*) were then analyzed to determine the best multiple linear regression model for suspended sediment concentration. The best model(s) were selected primarily on the basis of three statistics, adjusted r-squared ($R_a^2$), Mallow's *Cp*, and the maximum variance inflation factor (Max VIF). All three statistics indicate a regression model's goodness of fit, while also handicapping models that use a greater number of explanatory variables (Helsel and Hirsch, 2002). Results of the multiple linear regression analysis are shown in table 15.

Table 15. Linear multi-regression models for suspended sediment concentration. [U.S. Geological Survey samples only; $R^2$, goodness of fit; $R_a^2$, adjusted r-squared; *Cp*, Mallow's statistic; *Max VIF*, maximum variance inflation factor; $Q_A$, discharge normalized by watershed area; *Turb*, turbidity; $Q_{increase}$, change in $Q_A$ from 1 hour previous; $Q_{slope}$, percent change in $Q_A$ from 1 hour previous].

| | | | | | | | Dark gray cells indicate the variable is included in the regression model | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Model number | Number of variables | *Mean Squared Error* | $R^2$ | $R_a^2$ | *Cp* | *Max VIF* | $Q_A$ | *Turb* | $Q_{increase}$ | $Q_{slope}$ |
| 1 | 1 | 1,622.9 | 0.744 | 0.744 | 101.9 | - | | | | |
| 2 | 1 | 888.2 | 0.896 | 0.895 | 22.3 | - | | | | |
| 3 | 1 | 5,002.6 | 0.434 | 0.426 | 468.2 | - | | | | |
| 4 | 1 | 8,239.8 | 0.035 | 0.023 | 819.0 | - | | | | |
| 5 | 2 | 897.2 | 0.896 | 0.894 | 24.0 | 3.91 | | | | |
| 6 | 2 | 706.3 | 0.918 | 0.916 | 3.5 | 1.00 | | | | |
| 7 | 2 | 1,115.3 | 0.871 | 0.868 | 47.3 | 1.00 | | | | |
| 8 | 2 | 857.4 | 0.901 | 0.898 | 19.7 | 1.69 | | | | |
| 9 | 3 | 804.2 | 0.908 | 0.905 | 14.9 | 3.91 | | | | |
| 10 | 3 | 1,123.6 | 0.872 | 0.867 | 48.6 | 1.38 | | | | |
| 11 | 3 | 701.2 | 0.920 | 0.917 | 4.0 | 3.91 | | | | |
| 12 | 4 | 705.2 | 0.920 | 0.916 | 5.4 | 3.91 | | | | |

Multiple regression model no. 6, which uses turbidity and the slope of streamflow, is the best predictive model for suspended sediment concentration because it has the lowest *Cp* and *Max VIF* values and the second highest $R_a^2$ value. During periods when turbidity data are not available, such as prior to 2005 and periodically after 2005, the best regression model is no. 7, which has the lowest *Cp* and *Max VIF* values, and second highest $R_a^2$ values of the models that do not use turbidity.

A basis of comparison for the regressed suspended sediment concentration values is given by Gellis and others (2004), who used alternate linear estimation methods to calculate suspended sediment concentration for the South Fork Shenandoah River at Front Royal, Virginia (USGS station no. 01631000), about 100 mi downstream and to the northeast of the South River watershed. Their results show 50$^{th}$ and 90$^{th}$ percentile suspended sediment concentration values of 10.5 and 157 mg/L at monitoring station 01631000, which has a drainage area of 1,634 mi$^2$. Compared to the regressed values in this study, for the combined periods October 1, 1990, through September 30, 2000, and April 1, 2005, through March 31, 2007, Waynesboro (01626000) exhibits 50$^{th}$ and 90$^{th}$ percentile values of 1.7 and 19.3 mg/L, whereas Harriston (01627500) exhibits values of 3.4 and 42.3 mg/L, respectively. Because rivers with larger drainage areas have higher suspended sediment concentrations, the statistics for the regressed suspended sediment concentration values compare reasonably well (Gellis and others, 2004).

The regressed suspended sediment concentration time series from model no. 7 is shown in figure 13. There is reasonable agreement between the observed and regressed values, except at very low values where analytical detection limits are approached. The value of the regression method can be seen in the storm peak values of regressed suspended sediment concentration, which generally exceed the observed values. This is beneficial to the calibration because infrequent large storms carry most of the suspended sediment load, but grab samples are unlikely to have been collected at the moment of peak suspended sediment concentration values during a storm. The regression equation provides a means of extrapolating beyond the highest observed suspended sediment concentration values, although the extrapolated values have considerably less certainty than regressed values within the range of observed data.

**FIGURE 13 NEAR HERE**



## Meteorological and Climatic Data

The numerical watershed model requires a variety of climatic and meteorological input time-series data. Following Chesapeake Bay Community Watershed Model, Phase 5 (CBM5) structure, the following data were input to the model: precipitation, cloud cover, dew point, wind speed, solar radiation, air temperature, and potential evapotranspiration (Chesapeake Bay Program, 2006). These data all were in the form of time series with hourly time steps. HSPF uses these input data to calculate actual evapotranspiration, soil moisture storage, snow melt, and runoff, among other hydrologic variables.

For the period January 1985 through August 2005, time-series data for the above variables were obtained from the CBM5 model and used in the South River watershed model without modification, except for scaling potential evapotranspiration time-series data to improve the overall simulated water balance. The CBM5 climatic and meteorological time-series data were developed from observational data provided by the National Climatic Data Center of the National Oceanic and Atmospheric Administration. Observational data from over 200 hourly weather monitoring stations in the Chesapeake Bay watershed were integrated using statistical techniques to account for spatial and temporal gaps in the data, and to create continuous hourly time series (Chesapeake Bay Program, 2006). Only those time series applicable to the five land segments found in the South River watershed (A51015, A51165, A51820, B51015, and C51015) were used in this study.

Hourly climatic and meteorological time series for all areas of the model were extended through March 31, 2007, using the data from U.S. Air Force meteorological monitoring station 724105 at the Shenandoah Valley Regional Airport in Weyers Cave, 14 mi north of Waynesboro (fig. 11). Hourly surface observations at the Shenandoah Valley Regional Airport were obtained from the National Climatic Data Center website (http://www.ncdc.noaa.gov/oa/ncdc.html) for precipitation, dew point, wind speed, and air temperature. Cloud cover was estimated from hourly observations of sky cover (SKC), converting the observation codes as follows: clear (CLR) = 0.0, scattered clouds (SKT) = 3.0, partial obscuration (POB) = 6.0, broken (BKN) = 7.0, overcast (OVC) = 10.0, and obscured (OBS) = 10.0. Hourly solar radiation values were calculated from cloud cover and latitude using WDMUtil software (Hummel and others, 2001). The Hamon method (Hamon, 1961) was applied within WDMUtil to calculate potential evapotranspiration using latitude and daily minimum and maximum air temperatures.

Additional sources of precipitation data were available for 2005-07. Daily precipitation data were provided by Invista for its wastewater treatment plant in Waynesboro at the former DuPont plant site (Brenda Kennell, Invista, written commun., 2007) and daily precipitation data were downloaded from the National Climatic Data Center website for the City of Waynesboro sewage treatment plant (STP) (cooperative station ID# 448941). Daily precipitation totals recorded at the Waynesboro STP and at the Invista wastewater treatment plant were not used in compiling the CBM5 data (Chesapeake Bay Program, 2006) and differ from precipitation totals recorded at the Shenandoah Valley Regional Airport during the same period. The calibrated watershed model in this study uses precipitation data from all of these sources, with CBM5 data through August 2005 as the base and the additional data included where available to modify CBM5 values.

Observed precipitation for the period April 1, 2005, through March 31, 2007, at the three monitoring stations in the study area, as well as CBM5 estimated precipitation, is shown in figure 14. All of the observation data shown were collected using different procedures and in the case of the Waynesboro STP and the Invista site, were recorded on a daily, rather than hourly, basis. In addition to both the Waynesboro STP and Invista data showing an additional 20 in. of rain during the 2-year period, the storm patterns also show differences when compared to the Shenandoah Valley Regional Airport data. The most extreme example occurred during a storm on October 9, 2005, which shows up in the Invista and Waynesboro STP data as about 6 in. of precipitation, but only about 0.7 in. are observed in both the Shenandoah Valley Regional Airport and CBM-A51015 data. These differences indicate the potential for input errors to the HSPF model and are discussed in more detail later in the report.

**FIGURE 14 NEAR HERE**

## Point Sources

In the South River watershed model, point sources are flows of water and associated constituents that discharge directly to the river. A typical example is discharge from a wastewater treatment plant.

Data describing point-source discharges to the South River were compiled from the Virginia Pollutant Discharge Elimination System database that is maintained by the VDEQ for discharges in the State of Virginia. Of the 12 individually permitted facilities in the South River, 5 industrial or major municipal facilities were included in the model. Other smaller discharges were determined to contribute insignificant amounts of mercury to the South River. A detailed listing of data used to compile point-source discharge time series is given in Appendix 1.

Because data in the Virginia Pollutant Discharge Elimination System typically have monthly time steps, whereas the time series input to the South River watershed model have daily time steps, point-source data were disaggregated assuming constant daily rates within each month. Additional data with shorter time steps were collected, where possible, from discharge facility operators and used to supplement the Virginia Pollutant Discharge Elimination System data. When only annual data were available, these were disaggregated to daily intervals assuming seasonal patterns by month and constant daily rates within each month.

## Additional Model Flows to the River

Two discharges to the South River, specified in the model but not subject to permit regulations, are treated in the model as point-source flows to the river. These flows are from Frew Pond/Baker Spring and from Loth Spring, which are adjacent to the South River in Waynesboro, and are known to have large water flow rates (Brenda Kennell, Invista, written commun., 2007). Baker Spring flows into Frew Pond, which is a reservoir adjacent to the river at the plant site and managed by Invista. From Frew Pond, water flows over a weir and discharges to the South River. Loth Spring is adjacent to the river on its North side across from Frew Pond and flows directly to the river. Frew Pond/Baker Spring and Loth Spring are assigned monthly flow rates in the model on the basis of observed flows (DuPont Corporate Remediation Group, 2006a) and an assumed seasonal variation of 30 percent.

# Conceptual Model of Mercury Fate and Transport in the Watershed

As a foundation for building a numerical watershed model, a conceptual model for mercury fate and transport in the watershed was developed first. The conceptual model summarizes the primary paths by which mercury enters the South River water column and the fate of the mercury once it is in the river (fig. 15).

**FIGURE 15 NEAR HERE**

Mercury concentrations in all media are markedly higher downstream of the plant site than above it and it is presumed that most mercury currently (2009) entering the South River originated from the plant site at some time during or after 1929. It is known that the flood plain contains legacy mercury from the plant site and that contaminated sediment from the flood plain is currently entering the river. The Waynesboro monitoring station (01626000) is the only one of the three monitoring stations upstream of the plant site, and serves as a background reference station in this study.

At all three monitoring stations, filtered mercury concentrations in the water column increased with increasing streamflow as shown in figure 8. This observation is consistent with the hypothesis that contaminated sediments are the primary source of mercury in the water column. If point-source discharges were the primary Hg load, then river concentrations would be more likely to decrease with increased streamflow due to dilution effects.

Total mercury in the South River exhibits a partitioning ratio between dissolved and sorbed phases of about 1,000,000 (log Kd=6). The importance of partitioning to the TMDL is diminished by the fact that fish tissue methylmercury correlates strongly with the sum of filtered and particulate mercury, however, and the sum of the two concentrations is only secondarily affected by the exchange of mercury between sorbed and dissolved phases.

Several lines of evidence point to contaminated soil in the flood plain and river channel as the current greatest source of mercury to the river. Downstream surveys have shown that mercury concentrations in fish, water, and sediment rise steadily from the plant site downstream for about 12 mi (Turner and Jensen, 2006; Flanders and others, 2007). The relatively steady increase in concentrations points to mercury inputs being dispersed for many miles along the river rather than coming from discrete inputs such as point-source discharges or tributaries. Except for the sharp increase in water column mercury concentrations at the plant site, there are no abrupt THG increases that would indicate a major input of mercury from point sources. The accounting of mercury loads to the river also requires that a large percentage of mercury come from nonpoint sources to achieve a mass balance, as discussed in a later section, Mercury Transport Model Calibration Results.

# Watershed Model Development

A numerical watershed model of the South River watershed was developed to simulate dynamic streamflow response, sediment transport, and mercury transport. The simulation model calculates mass balances for water as well as sediment and mercury in the South River for the simulation period January 1, 1985, through March 31, 2007. The simulation model also permits hypothetical conditions, such as reduced mercury source loads, droughts, floods, or long-term mercury mass balances, to be analyzed.

The software used to implement the numerical model is Hydrological Simulation Program – FORTRAN (HSPF), a watershed-based modeling package widely used for TMDL development (Bicknell and others, 2001; Donigian and others, 1995). The hydrologic component of HSPF generates time series of streamflow in response to precipitation, evapotranspiration, and movement of water from the land surface through various routes to streams. Simulations are transient and require extensive input data describing land use and hydraulic characteristics, climatic conditions, river geometry, and sediment and mercury transport characteristics.

The first 6 years of the South River watershed model simulation (1985 through 1990) bring the model to relative steady state conditions, dampening perturbations from initial conditions. A 10-year period, from October 1, 1990, through September 30, 2000, was used to calibrate the hydrologic and sediment parts of the model. The five years from October 1, 2000, through September 30, 2005, were used to verify the calibrated hydrologic and sediment parts of the model. The mercury transport model was calibrated for the period April 2005, through March 2006, and verified for the period April 2006, through March 2007.

The South River watershed model has a 1-hour time step, which is sufficiently small to represent important hydrologic changes, but not so small as to make model run times impractical. The calibrated watershed model requires run times of about 4 minutes.

## Functional Description of Hydrological Simulation Program – FORTRAN (HSPF)

HSPF is a mathematical model designed to simulate the hydrology and movement of contaminants in a watershed. As applied to the South River watershed, the HSPF model simulates streamflow, sediment transport, and mercury transport. HSPF calculates water, sediment, and contaminant loads following mass conservation principles of water, with inflow equaling outflow plus or minus any change in storage (Zarriello and Bent, 2004). In HSPF, a watershed is represented by a collection of hydrologically similar areas, referred to as hydrologic response units (HRUs), which drain into a network of stream or lake segments. Each HRU represents land having characteristic hydrologic controls, such as land use, soil, subsurface geology, and other factors deemed important in controlling hydrology. Each stream segment represents a river reach or lake. For each HRU and stream segment, the model computes a water budget (inflows, outflows, and changes in storage) for each time step.

HRUs represent either pervious or impervious land areas. Both pervious and impervious land areas can retain precipitation on the surface. On pervious land areas, excess precipitation can infiltrate to the subsurface, where storages and fluxes are calculated for upper and lower ground-water zones, or can run off to a river reach. On impervious area, all water that is not evaporated from the surface produces runoff to a river reach. The downstream end of each river reach is referred to as a node. Nodes are typically placed to define channel segments with similar physical properties, or at other locations where estimates of streamflow or contaminant concentrations are desired. The hydrologic characteristics used for kinematic wave routing of water in a river reach are defined in a function table that is specified in the model input.

The SCHEMATIC and MASS-LINK blocks define the physical layout of the watershed, linking river reaches together and assigning the acres to each pervious and impervious land area.

The inflows to and outflows from a river reach in the South River watershed model are shown in figure 16 (modified from Zarriello and Bent, 2004, fig. 9). Surface runoff can discharge to a reach from impervious surfaces and pervious surfaces. Infiltrated water can discharge to a reach through the subsurface as interflow, a fast-responding shallow subsurface flow, or from active ground water, a slow-response base-flow component. Inflow to a reach can also come from upstream reaches, direct precipitation, and other user-specified sources such as treated point-source discharges.

**FIGURE 16 NEAR HERE**

HSPF requires two primary input files for its operation, the user control input file and the watershed data management file. The user control input file directs the model-process algorithms and sets user-specified input variables. The watershed data management file holds a time-series database. Time-series datasets are organized in the South River watershed data management file as shown in table 16. A more complete description of the HSPF software is given in the "HSPF User's Manual" (Bicknell and others, 2001).

Table 16. Organization of dataset numbers in the watershed data management file for the South River watershed model, Virginia.

| DSN | Purpose |
|---|---|
| 1101-1523 | Simulated daily AGWO output, last 3 digits are hydrologic response unit number. |
| 2101-2523 | Simulated daily IFWO output, last 3 digits are hydrologic response unit number. |
| 3000-3999 | Observed/calculated meteorological inputs. |
| 4000-4999 | Simulated hydrologic and sediment outputs. |
| 5000-6015 | Simulated mercury concentration, storage, and load outputs. |
| 6101-6999 | Point-source flow and load inputs. |
| 7000-7999 | Simulated daily sediment runoff output, last 3 digits are hydrologic response unit number. |

## Representation of the Watershed

The South River watershed is represented in the HSPF model as a combination of HRUs, consisting of pervious and impervious land surfaces. Each HRU has an assigned contributing area to each stream reach. The stream reaches are linked to each other in downstream order. Basin and sub-basin boundaries in the model study area were initially obtained from the Chesapeake Bay HSPF model Phase 5.14, referred to here as "CBM5", developed by the USEPA, the USGS, and other partners (Martucci and others, 2005; Chesapeake Bay Program, 2006).

The South River watershed is divided into five model sub-basins that each contains a single river reach (fig. 17). The nodes defining the sub-basins were selected to correspond with monitoring locations along the South River so that output from the model could be compared to field observations at the same locations. Each sub-basin is composed of multiple HRUs, which send their output (water, sediment, and mercury) to the river reaches. The CBM5 model has four sub-basins within the South River watershed (PS2_6730_6660, PS2_6660_6490, PS2_6490_6420, and PS2_6420_6360). For this study, an additional sub-basin was needed to produce simulation results at the location of streamflow-gaging station 01626920.

Using geographic information system (GIS) software, one of the CBM5 sub-basins (PS2_6490_6420) was divided into sub-basins 3 and 4 in the South River watershed model (fig. 17). River reach parameters and HRU areas contributing to each reach were then recalculated.

**FIGURE 17 NEAR HERE**



Parameters describing hydrology, sediment transport, and mercury transport were assigned to each HRU. Initial parameter values were set equal to those in the calibrated CBM5 model. The CBM5 model parameters had already been calibrated to streamflow values from 1985 through 2005, including streamflow on three of the South River streamflow-gaging stations (01626000, 01626850, and 01627500). Some model parameters were then modified in this study to improve the match between simulated and observed streamflow, sediment concentrations, and mercury concentrations. These changes are discussed in the following sections describing calibration of the model.

## Development of Hydrologic Response Units (HRUs)

The smallest HSPF model component is the HRU. Within a single HRU, climatic conditions, hydrologic responses, and contaminant transport are assumed to be uniform. The HRUs in the South River watershed model are nearly identical to those used in the CBM5 model (Martucci and others, 2005). These HRUs are based on county boundaries, land use, and valley or mountain geography. Five land-county segments developed for the CBM5 model are present in the South River (fig. 18). Climatic variables and precipitation vary according to land-county segment. There are 25 CBM5 land-use types in the watershed, and an additional land use, mercury-contaminated flood plain, was added for this study (table 17). The five land-county segments combined with the 26 land uses result in 130 different HRUs in the South River watershed. Fifteen of the HRUs are impervious land areas, and 115 are pervious areas.

**FIGURE 18 NEAR HERE**



Table 17. Land-use representation in the watershed model, South River, Virginia. [IMPLND, impervious land area; PERLND, pervious land area; HRU, hydrologic response unit]

| HRU Type | Land Use | Sub Basin Area (acres) 1 | 2 | 3 | 4 | 5 | Total (acres) |
|---|---|---|---|---|---|---|---|
| IMPLND | animal feeding operations | 20 | 7 | 1 | 13 | 51 | 92 |
| IMPLND | low intensity impervious urban | 352 | 865 | 53 | 76 | 99 | 1,444 |
| IMPLND | high intensity impervious urban | 113 | 263 | 3 | 25 | 32 | 436 |
| PERLND | forest | 48,816 | 5,885 | 5,862 | 15,817 | 6,090 | 82,470 |
| PERLND | harvested forest | 493 | 64 | 63 | 175 | 73 | 868 |
| PERLND | alfalfa | 1,221 | 0 | 162 | 520 | 76 | 1,979 |
| PERLND | natural grass | 1,865 | 1 | 3 | 13 | 11 | 1,892 |
| PERLND | high till without manure | 18 | 1 | 2 | 8 | 5 | 33 |
| PERLND | high till with manure | 259 | 11 | 36 | 114 | 125 | 544 |
| PERLND | hay without nutrients | 538 | 22 | 59 | 254 | 152 | 1,026 |
| PERLND | hay with nutrients | 2,371 | 98 | 261 | 1,118 | 626 | 4,475 |
| PERLND | low till with manure | 1,293 | 54 | 178 | 574 | 439 | 2,537 |
| PERLND | nutrient management alfalfa | 262 | 61 | 43 | 137 | 251 | 754 |
| PERLND | nutrient management high till w/manure | 176 | 7 | 24 | 78 | 57 | 342 |
| PERLND | nutrient management high till wo/manure | 12 | 1 | 2 | 5 | 3 | 22 |
| PERLND | nutrient management hay | 1,611 | 67 | 232 | 704 | 333 | 2,946 |
| PERLND | nutrient management low till | 879 | 36 | 97 | 414 | 217 | 1,642 |
| PERLND | nutrient management pasture | 453 | 380 | 87 | 375 | 1,103 | 2,397 |
| PERLND | pasture | 16,042 | 302 | 1,727 | 7,401 | 2,287 | 27,759 |
| PERLND | bare-construction | 369 | 548 | 26 | 101 | 95 | 1,138 |
| PERLND | extractive | 92 | 3 | 0 | 7 | 2 | 103 |
| PERLND | trampled | 83 | 3 | 12 | 34 | 17 | 149 |
| PERLND | nursery | 210 | 9 | 32 | 90 | 31 | 372 |
| PERLND | high intensity pervious urban | 2,541 | 956 | 225 | 606 | 404 | 4,732 |
| PERLND | low intensity pervious urban | 1,230 | 3,484 | 513 | 538 | 810 | 6,576 |
| PERLND | mercury-contaminated flood plain | 0 | 493 | 378 | 1,412 | 1,105 | 3,388 |
| | Total Acres | 81,316 | 13,619 | 10,082 | 30,606 | 14,493 | 150,115 |

Pervious areas occupy 98.7 percent of the watershed. Forestry and agriculture are the dominant land uses, representing 55.5 percent and 31.2 percent, respectively of the total watershed area. Impervious surfaces in the watershed consist primarily of developed urban areas with dense building and pavement cover and make up 1.3 percent of total watershed area. All pervious and impervious areas in the model contribute their outflows directly to a stream reach.

All HRUs were defined according to the CBM5 scheme, with one exception. Five pervious land areas were created to represent mercury-contaminated flood plains. Areas for the five pervious land areas representing mercury-contaminated flood-plain areas were calculated from spatial data outlining the 62-year flood plain. The 62-yr floodplain represents the maximum extent of the floodplain inundated since mercury was originally released from the former Dupont plant site. The largest daily flow recorded since release of mercury was determined by flood frequency analysis to have a return period of 62 yrs. Hydraulic analysis was then conducted to delineate the floodplain area inundated by a flood of this magnitude (DuPont Corporate Remediation Group, 2007).

## Stream Reaches

River reaches receive their input from pervious land areas, impervious land areas, and upstream reaches, while discharging either to a downstream reach or to the model exit (fig. 15). The watershed model contains five stream reaches, one for each sub-basin. Model parameter values for each reach were initially set to be the same as those in the CBM5 model. Reach PS2_6490_6420 in the CBM5 model was divided into reaches 3 and 4 of this study's model, so that simulation results at streamflow-gaging station 01626920 could be obtained.

The physical characteristics of the five South River watershed model river reaches are listed in table 18. Parameters were adjusted during the calibration process, including the length and elevation drops, to improve hydrologic and sediment transport simulations. These parameters were reset to values determined by GIS analysis of 10-m digital elevation model data. The FTABLES, which specify channel geometry, were not changed from the CBM5 model.

Table 18. River reach characteristics in the calibrated South River watershed model. [mi, miles; no., number; USGS, U.S. Geological Survey].

| Model River Reach Number | Extent | | Upstream Reach Number | Length mi | Elevation Drop feet | Slope |
|---|---|---|---|---|---|---|
| | From | To | | | | |
| 1 | headwaters | USGS station no. 01626000 | none | 14.3 | 164 | 0.0022 |
| 2 | USGS station no. 01626000 | USGS station no. 01626850 | 1 | 5.1 | 46 | 0.0017 |
| 3 | USGS station no. 01626850 | USGS station no. 01626920 | 2 | 3.0 | 20 | 0.0013 |
| 4 | USGS station no. 01626920 | USGS station no. 01627500 | 3 | 11.3 | 98 | 0.0017 |
| 5 | USGS station no. 01627500 | South Fork Shenandoah River | 4 | 7.7 | 105 | 0.0026 |

## Hydrologic Model

The hydrologic component of the model simulates water movement and storage in the South River watershed. Precipitation and point-source discharges to the river are the only hydrologic inputs to the model domain whereas actual evapotranspiration and streamflow are the only outputs. Precipitation that falls on the land surface but does not evaporate or transpire is routed to the river. Once in the river, water moves downstream and exits the model from the last river reach (number 5). Major components of the hydrologic cycle simulated by HSPF for pervious land areas and river reaches are shown in figure 19. More detailed descriptions of the storage and flow terms can be found in Bicknell and others (2001).

**FIGURE 19 NEAR HERE**

## Point-Source Discharges

Reaches 1, 2, 3, and 5 receive discharges from point sources. The discharges come from a variety of permitted facilities, listed in table 19 and Appendix 1. Other small facilities discharge to the South River but were not included in the model because they have flows of less than 0.5 million gallons per day (Mgal/d) and discharge insignificant amounts of mercury. Discharge rates, suspended sediment concentrations, and mercury concentrations were assigned outside of the model and input to the model as time series with daily time steps. The data available to describe each point source varied widely and were from a variety of sources. Time series describing the point-source discharges were developed in collaboration with Invista, DuPont, and the VDEQ.

Table 19. Point sources in the South River watershed model, average flow, sediment loads, and mercury loads for the period April 1, 2005, through March 31, 2007. [VAPDES, Virginia Pollutant Discharge Elimination System; NPDES, National Pollutant Discharge Elimination System; HG, mercury; g, grams; $ft^3/s$, cubic feet per second; STP, sewage treatment plant; na, not applicable]

| Point Sources in Model | | | VAPDES NPDES Permit Number | Annual Mean (2005-2007) | | |
|---|---|---|---|---|---|---|
| Model ID | Facility name, downstream order | Model Reach | | Flow ($ft^3/s$) | Sediment Load (Ton) | HG Load (g) |
| 101 | Stuarts Draft STP | 1 | VA0066877 | 1.671 | 1.5 | 1.0 |
| 222 | Loth Spring | 2 | na | 1.756 | 1.5 | 6.4 |
| - | INVISTA/ former DuPont | - | - | | | |
| 201 | outfall 001 | 2 | VA0002160 | 6.523 | 17.2 | 402.9 |
| 203 | outfall 003 | 2 | VA0002160 | 0.066 | 0.4 | 2.8 |
| 204 | outfall 004 | 2 | na | 0.014 | 0.3 | 0.5 |
| 208 | outfall 008 | 2 | na | 0.374 | 4.2 | 89.0 |
| 209 | outfall 009 | 2 | na | 0.111 | 0.8 | 8.1 |
| 210 | outfall 010 | 2 | na | 0.040 | 1.9 | 8.2 |
| 211 | outfall 011 *(after 08/02)* | 2 | VA0002160 | 0.020 | 0.4 | 21.8 |
| 212 | outfall 012 | 2 | na | 0.000 | 0.0 | 0.0 |
| 213 | outfall 013 | 2 | na | 0.007 | 0.0 | 0.3 |
| 214 | outfall 014 | 2 | na | 0.005 | 0.0 | 0.3 |
| 221 | Frew Pond, Baker Spring | 2 | na | 7.025 | 5.9 | 25.4 |
| 231 | Plant Site Ground-water Discharge | 2 | na | 0.501 | 0.0 | 1.5 |
| - | *INVISTA/ former DuPont* | *Plant Site Totals* | | *15* | *31* | *561* |
| 241 | Waynesboro STP | 2 | VA0025151 | 5.497 | 42.2 | 37.1 |
| 301 | Genicom | 3 | VA0002402 | 0.196 | 0.0 | 0.0 |
| 501 | Alcoa | 5 | VA0001767 | 2.486 | 12.7 | 40.6 |
| | | | Totals | 26 | 89 | 646 |

# Sediment Transport Model

Sediment transport was incorporated into the watershed model because most mercury transport occurs in association with suspended sediment. At both the Dooms and Harriston monitoring stations, water-sample analyses indicate that over 95 percent of the mercury in the water column is sediment-associated, with suspended sediment defined as material not passing a 1.5-$\mu$m filter.

In the watershed model, sediment moves to the river from impervious and pervious land areas during surface runoff events (fig. 20). Sediment loads from land surfaces vary according to land use and location in the watershed. The South River watershed model simulates sediment transport in the river using the same parameterization as the CBM5 model (Chesapeake Bay Program, 2006); with a power function governing sand transport and critical stress levels controlling silt and clay transport. Sediment transport parameter values were initially assigned to be the same as those in the CBM5 model and were then modified during the calibration process. Sediment transport is handled differently for impervious land areas, pervious land areas, and river reaches as described in the next section(s) (fig. 21).

**FIGURE 20 NEAR HERE**

**FIGURE 21 NEAR HERE**

## Impervious Land Area Sediment Transport

Sediment transport from impervious land surfaces to river reaches is simulated using the IMPLND-SOLIDS module. At each hourly time step, solids accumulate or are removed, by street cleaning for example, from the land surface at the user-specified rates listed in Appendix 2. Solids are transported from impervious land areas to river reaches, at user-specified exponential rates, when overland flow occurs. Parameters governing sediment production from each impervious land area were initially assigned CBM5 values, and then calibrated by matching simulated to observed suspended sediment concentration values, as described in a later section of this report, Sediment Transport Model Calibration Results.

## Pervious Land Area Sediment Transport

Simulation of sediment transport to the river from each pervious land segment is performed by the PERLND-SEDMNT module. Only detached sediment is available to be transported to the river, therefore, no scouring is simulated. Sediment can be detached by soil drying, rainfall splash, or other processes at detachment rates specified by the user. Detached sediment is transported to the river during overland flow runoff events at exponential rates controlled by user-specified coefficients. Sediment transport from the five pervious land areas representing mercury-contaminated flood-plain areas is simulated using the same processes and simulation modules. Final calibrated values for sediment transport parameters are listed in Appendix 2.

## Sediment Point Sources

Municipal and industrial discharges to the river generally contain suspended sediment. These point sources are treated in the model as direct inputs to the river with sediment loading rates specified outside of the model. These rates were determined from data collected by discharge permit owners and stored in the Virginia Pollutant Discharge Elimination System database. Point sources contribute only a very small percentage (less than 1 percent) to the total sediment load of the South River. Summaries of the sediment point-source loads are listed in table 19 and Appendix 1.

## Sediment Transport in the River

Sediment entering a river reach can be deposited and remain stationary on the channel bed or travel downstream in suspension. Transport, deposition, and resuspension of sediment within a river reach are handled in HSPF by the modules shown in figure 21. At each hourly time step, HSPF recalculates all sediment storage and load terms. Suspended sediment present in a river reach can settle to the channel bottom, exit downstream, or remain in the reach. Sediment deposited on the channel bottom can be resuspended by increased flow velocities. Initial conditions are user-specified for initial suspended sediment concentration and for depth of sediment on the bed of each river reach.

Sediment within a river reach is divided by HSPF into three sediment size classes -- sand, silt, and clay. Transport of each size class is simulated separately. Non-cohesive particles (sand) and cohesive particles (silt and clay) have different algorithms controlling transport within the river. There were insufficient data from the South River to accurately calibrate to suspended sediment size so sediment size fractions in the model were assigned to be 33.3 percent sand, 33.3 percent silt, and 33.3 percent clay. The capacity of each river reach to transport sand downstream is calculated using an exponential equation (Bicknell and others, 2001) with user-specified rates. When transport capacity exceeds the rate of sand transport, resuspension of bed sand occurs. Conversely, when sand load exceeds transport capacity, deposition of sand on the channel bed occurs. Silt and clay transport are simulated with a different algorithm that controls scour and deposition according to user-specified settling rates, critical stress thresholds for deposition and suspension, and erodibility coefficients. Values for sand, silt, and clay transport parameters used in the calibrated South River watershed model are listed in Appendix 2.



## Mercury Transport Model

The third component of the South River watershed model simulates mercury transport on the basis of the conceptual model described earlier. Total mercury is the only form of mercury that was simulated. Other forms of mercury such as methylmercury were not simulated, not because they are absent or unimportant, but because the dynamics of methylmercury cycling and bioaccumulation in the South River system are currently not well understood. Modeling of total mercury in the South River was performed because fish tissue methylmercury concentrations correlate more strongly with total mercury than with any other form of mercury in the water column, including methylmercury (Virginia Department of Environmental Quality, 2008b). The model is constructed so that future studies can incorporate methylmercury cycling, bioaccumulation, or other processes if desired.

Mercury is transported to the river along multiple hydrologic pathways: direct precipitation to the river surface, point-source discharges, ground water and interflow, land-surface sediment runoff, channel margin inputs, and downstream advection. The HSPF modules used to simulate these pathways are listed in table 20 and shown in figure 22. Once mercury enters a river reach, it partitions between dissolved and sorbed phases. The model simulates the storage of mercury in channel bed sediment and the reintroduction of mercury to the water column when bed sediment is resuspended by higher flows.

Table 20. Modules in Hydrologic Simulation Program-FORTRAN used to simulate mercury transport. [Hg, mercury; PERLND, pervious land area; IMPLND, impervious land area; RCHRES, river reach]

| **Mercury Source/Process** | **HSPF Module(s)** |
|---|---|
| Ground Water | PERLND>PQUAL>QUALGW |
| Interflow | PERLND>PQUAL>QUALIF |
| Sediment Hg in Runoff | PERLND>PQUAL>QUALSD and IMPLND>IQUAL>WASHSD |
| Precipitation Hg on River | RCHRES>CONS |
| Hg Point Sources | EXT SOURCES |
| Instream Sorption/Desorption | RCHRES>GQUAL>ADSDES |
| Downstream Advection | RCHRES>GQUAL>ADVECT (Dissolved Hg)<br>RCHRES>GQUAL>ADVQAL (Sediment associated Hg) |
| Channel Margin Inputs | PERLND>PWAT and MASS-LINK |

**FIGURE 22 NEAR HERE**

Silt and clay particles are assigned the same mercury transport parameters and initial $THG_{SS}$ concentrations. Sand in the model is assumed to have a sorption capacity for mercury that is 1,000 times lower than that of silt or clay because sand typically has a much lower sorption capacity than silt or clay.

## Mercury Sources to the River

Mercury sources to the South River that were known as of April 1, 2007 were included in the watershed model. The sources are listed in table 21 and discussed separately below. For mercury sources that are relatively well described by observation data, model concentrations were either held constant or were minimally adjusted during the calibration process. Relatively well-described sources include point sources and direct precipitation to the river. Other mercury sources that are less well described by data include ground water, interflow, concentrations on runoff sediment, and channel margin inputs, all of which had greater adjustments during the model calibration process.

Table 21. Mercury sources to the South River in the watershed model. [Hg, mercury; THG, total mercury; $THG_F$, aqueous filterable total mercury; $THG_{Sed}$, total mercury on soils or surface sediment; USEPA, U.S. Environmental Protection Agency; VPDES, Virginia Pollutant Discharge Elimination System; ng/L, nanograms per liter; μg/g micrograms per gram; HRU, hydrologic response unit]

| **Hg Source to South R.** | **Data Used to Determine Initial Concentrations** | **Model Input** |
|---|---|---|
| Atmospheric deposition on river surface. | USEPA (USEPA,2007) | Precipitation HG concentration = 21.8 ng/L |
| Ground water from uncontaminated land areas. | $THG_F$ concentrations at Waynesboro gage (01626000) | Ground-water dissolved HG concentration= 0.7 ng/L |
| Ground water from HG contaminated flood plain. | Flood-plain ground-water samples, plus calibration | Ground-water dissolved HG concentration = 1.3-2.9 ng/L |
| Interflow | Precipitation $THG_F$ (USEPA,2007) and calibration | Calibrated values from 10.0 to 16.7 ng/L |
| Sediment attached HG runoff from uncontaminated pervious and impervious land surfaces. | Sediment samples from uncontaminated areas | $THG_{Sed}$ concentration = 0.07 μg/g for all uncontaminated HRUs |
| Sediment attached HG runoff from contaminated pervious land surfaces. | Sediment samples within respective reaches | $THG_{Sed}$ concentration varies by reach and HRU from (7.6 to 16.7 μg/g) |
| Point-source discharges. | VPDES flow data, grab sample analyses for minor sources, routine base-flow and stormflow monitoring of former DuPont plant site | Point-source flow rates and concentrations to river (model river reach 1, 2, 3, and 5) |
| Channel margin inputs. | THG concentrations at Waynesboro (01626000), Dooms (01626920), and Harriston (01627500) | Input of sediment attached HG to water column of each model river reach, using MASS-LINK block |

## Atmospheric Deposition

It is assumed that precipitation falling directly on the river has a dissolved mercury ($THG_F$) concentration equal to 21.8 ng/L, which is the average HG concentration in precipitation discussed earlier in this report. The model indirectly accounts for atmospheric mercury deposited on land surfaces by assigning mercury concentrations to hydrologic and sediment loads leaving the land surface. This approach allows more accurate mass balancing of mercury, and indirectly accounts for the processes of mercury cycling through soils, vegetation, animals, and atmospheric evasion.

## Land-Surface Runoff

All land surfaces in the model have runoff sediment with associated mercury. Runoff sediment $THG_{Sed}$ concentrations varied by reach and HRU. Sediment from uncontaminated areas was initially assigned a $THG_{Sed}$ value = 0.127 μg/g, the average mercury concentration on suspended sediment at the Waynesboro monitoring station. During the calibration process, this value was lowered to 0.07μg/g. Land surfaces known to be contaminated with mercury (such as 62-year flood-plain areas downstream of the plant site) were assigned higher runoff sediment $THG_{Sed}$ mercury concentrations, between 7.6 and 16.7 μg/g, to correspond with the observational data shown in table 13. These $THG_{Sed}$ concentrations for runoff sediment from contaminated areas were not changed during the calibration process, but loading coefficients controlling the amount of runoff sediment reaching the river were adjusted.

Model river reach 1 receives no runoff from contaminated flood-plain land areas. Model river reaches 2-5 are all at least partially downstream from the plant site, and receive sediment from both contaminated flood plains (determined from the 62-yr flood plain) and uncontaminated land surfaces. The watershed model accounts for the acreage of each HRU contributing to each model river reach.

## Ground Water and Interflow

Pervious land areas contribute mercury to river reaches through ground-water and interflow discharge (AGWO and IFWO). All mercury in AGWO and IFWO is assumed to be in the dissolved phase ($THG_F$). Impervious land areas have no ground-water or interflow discharge.

Ground water from all uncontaminated pervious land areas was assumed to have the same $THG_F$ concentration value. This was initially assigned to be 0.49 ng/L, the average base-flow $THG_F$ concentration at the Waynesboro monitoring station above the plant site. In the final calibrated model this value was adjusted to 0.7 ng/L. Ground water from contaminated pervious land areas was assigned $THG_F$ concentrations of 2.9 ng/L for model river reach 2, 3, and 4 and 1.3 ng/L for model river reach 5. Interflow $THG_F$ concentrations were assigned initial values between those of precipitation, 21.8 ng/L, and AGWO $THG_F$ concentrations. During calibration these were slightly adjusted and final IFWO $THG_F$ concentrations ranged from 10.0 to 16.9 ng/L.

## Point-Source Discharges

All point-source discharges in the model were assigned dissolved mercury concentrations. The actual point sources in most cases do carry sediment-associated mercury but limited monitoring data did not permit distinguishing between dissolved and sorbed phases for most of the point sources. Mercury point-source inputs are partitioned by the model between dissolved and sorbed phases within a single time step once they enter the river. Mercury loads from point sources and the data used to assign flow rates and concentrations are listed in table 19 and Appendix 1.

There were extensive monitoring data describing discharges from the former DuPont plant site and the other discharge facilities (DuPont, 2003a, 2006a, 2006b; Brenda Kennell, Invista, written commun., 2007). There were time gaps in the data and differences in monitoring frequency and reporting formats, however, the data were reformatted, disaggregated, and extrapolated where needed to produce daily values for the full simulation period. These data and the statistical treatments applied are summarized in Appendix 1.

## Riverbank and Channel Margin Inputs

During model calibration, it was observed that the model could not reproduce high observed THG concentrations during low and moderate flow periods, when only the mercury sources listed in the first six rows of table 21 were included in the model. An additional mercury load of roughly 100-200 kg/yr to the river was needed to calibrate the model. Model results discussed later in this report indicate that ground-water and interflow discharge to the river could not provide 100-200 kg/yr of mercury to the river without assigning them unreasonably high concentrations of mercury. The additional mercury entering the South River is most likely coming from contaminated channel margin sediment deposits. A variety of possible mechanisms could move mercury in these contaminated channel margin sediments to the river: bank erosion, bank collapse, disturbance of sediment by animals or fishermen or boaters, diffusion of mercury from contaminated sediment in contact with the water column, tree falls, ecological extraction of mercury from channel sediment, sediment displacement by interflow and ground-water discharge, hyporheic flow, desorption due to changed pH or oxidative state, another unknown mechanisms, or some combination of these, all of which could operate along the length of the river.

Bank retreat could account for much of the missing mercury load. Rhoades and others (2009) found that, on average, 109 kg/yr of mercury enters the South River from bank retreat, based on long-term erosion profiling and sampling of bank sediment. Bank collapse may work in concert with other mechanisms to produce mercury load to the river. Collapsed riverbank sediment could release mercury to hyporheic flow or ground-water discharge passing through it, for example. Sampling of pore water in surface sediment adjacent to the river during this study found elevated $THG_F$ concentrations at several locations downstream of the plant site (table 11). Evidence of mercury input to the river from banks was also seen by Turner and Jensen (2007), who found river reaches where water column mercury concentrations were higher near the bank than in the center of the river, implying an active source of dissolved mercury close to the banks.

The exact mechanism responsible for the additional mercury source along the South River is not known. Therefore, a relatively simple approach was taken in the model. MASS-LINK tables were added to create Hg-contaminated sediment inputs to the river reaches. Inputs were scaled with ground-water discharge (AGWO) and interflow (IFWO) from HG-contaminated pervious land areas. Ground-water and interflow rates provide signals of hydrologic conditions that are responsible for at least some of the wetting and hydraulic stress factors controlling bank collapse (Knighton, 1998). Loading coefficients were adjusted during the calibration process so that simulated THG concentrations in the river at the Dooms and Harriston monitoring stations matched observations. Channel margin inputs are treated separately from dissolved Hg ground-water and interflow inputs and separately from sediment-associated Hg in pervious land area and impervious land area runoff.

## Mercury Transport Within the River

In the simulations, mercury in the water column moves downstream both in the dissolved phase and sorbed to suspended sediment. When suspended sediment with sorbed mercury settles out of the water column onto the channel bed, the sorbed mercury remains with the sediment until it is resuspended. When sediment exits a reach, the associated mercury also exits.

HSPF partitions mercury in the water column by transferring it between dissolved and sorbed phases so that dissolved and sorbed concentrations approach an equilibrium ratio. The phase transfer is limited by a user-specified rate coefficient so that equilibrium partitioning is not instantaneous. A finite difference expression of the mercury continuity equation (equation 1) is solved for each reach at each time step to calculate the mass transfer between phases. The phase transfer is calculated separately for each size fraction (sand, silt, clay) of the suspended sediment. No transfer is simulated between sediment of different size classes, between bed sediment and ground water, or between bed sediment and the water column. Decay or production of mercury from other constituents are likely negligible, and therefore they were not simulated.

$$-d(RSED*SQAL)/dt + RSED*KT*(KD*DQAL - SQAL) = 0 \qquad \text{Equation 1}$$

where:

*RSED* = quantity of sediment in the model river reach (mass);
*SQAL* = concentration of constituent on sediment (mass Hg/mass sediment);
*DQAL* = concentration of dissolved constituent (mass Hg/volume water);
*KD* = distribution coefficient; and
*KT* = rate transfer coefficient.

A single distribution coefficient of 1,000,000 L/kg (liters per kilogram) is used to partition mercury between the aqueous phase and sorbed phase on suspended silt and clay. This value is based on ratios of $THG_{Sed}$ and $THG_F$ concentrations listed in tables 7 and 8 and batch tests results from Mason (2006). HSPF also requires a distribution coefficient for mercury sorption to sand and a lower coefficient of 1,000 L/kg is assumed. To ensure nearly instantaneous transfer of mercury between phases, a high rate transfer coefficient of 25.0 was used for partitioning between all suspended sediment size fractions and the water column. Mercury partitioning between channel bed sediment and the water column was slowed to almost zero by assigning a low rate transfer coefficient (0.0001) for all sediment-size fractions. This was done because *in-situ* partitioning of mercury between channel bed sediment and pore water is not well understood for the South River.

## Watershed Model Results

After compiling input data, the numerical watershed model was tested and calibrated. Model calibration, or the adjustment of model parameter values to achieve better agreement between observed and simulated values, was performed sequentially for streamflow, suspended sediment transport, and mercury transport. The streamflow and sediment transport calibration covered the period from water year 1991 through water year 2000 (October 1, 1990, through September 30, 2000). For mercury, the model calibration covered the period from April 2005 through March 2006, which corresponds with the period of intense mercury data collection. Model verification, in which results from the calibrated model are compared to observations for a separate period with the same model fit targets as used for calibration, was also performed. For streamflow and sediment transport, verification covered the period from water years 2001 through 2005, whereas for mercury, verification covered the period from April 2006 through March 2007.

As described in a previous section, Representation of the Watershed, all hydrologic and sediment model parameters were initially assigned values from the calibrated CBM5 model and were then adjusted to achieve a closer fit between simulated and observed values. Most of these changes were relatively minor because the CBM5 model parameters were previously calibrated. The CBM5 model does not simulate mercury; therefore, mercury transport parameters were assigned independently.

Improvements to the South River watershed model hydrology and sediment parameters were made by using additional data that were not available during the CBM5 calibration effort. CBM5 parameter values were calibrated using observed streamflow both outside and within the South River watershed. In the CBM5 model, for example, evaporation coefficients for land-county segment A51015 were optimized using streamflow observations from the South River streamflow-gaging stations (0162600, 01626850, 01627500) as well as stations on the Middle River (01624800, 01625000). Because this study focuses on the South River, parameter values were changed to obtain a better fit for only the South River observed streamflow values. Additional justification for modifications to the CBM5 parameters include the division of CBM5 RCHRES PS2_6490_6360 into reaches 3 and 4 in this model, and the availability of more recent streamflow and suspended sediment concentration data.

## Streamflow Model Calibration Results

The ability of the model to accurately simulate streamflow was evaluated by statistically comparing simulated and observed streamflow with respect to annual and seasonal water budgets, high-flow and low-flow distribution, and stormflow volumes. These comparisons were performed primarily using Expert System for the Calibration of the Hydrological Simulation Program– FORTRAN (HSPEXP) (Lumb and others, 1994).

The hydraulic component of the South River watershed model simulates the period January 1, 1985, through March 31, 2007, using hourly time steps. The 10-year calibration period includes the wettest year (1998) and the fourth driest year (1999) on record for the Harriston streamflow-gaging station. Observed mean annual flows at the Harriston streamflow-gaging station for years with complete data are shown in figure 23. A 2-year verification period from April 1, 2005, through March 31, 2007, was used to verify that the calibrated hydrology model can accurately simulate other time periods.

**FIGURE 23 NEAR HERE**

Hydraulic parameter values were adjusted during calibration to match observed and simulated water volumes. Changes to initial CBM5 parameter values were made to reduce the amount of runoff (table 22). Changes were made to the actual evapotranspiration coefficients that scale the External Source EVAP time series to improve simulated runoff volumes and to parameters INFILT and AGWETP to improve the distribution of runoff volumes between high- and low-flow periods. Final calibrated values for these parameters are listed in Appendix 2. The actual evapotranspiration multiplier coefficients used to scale evaporation input time series were increased by an average of 16 percent to better match observed total runoff. Parameter values for INFILT, which controls infiltration capacity, were reduced uniformly by 50 percent to reduce runoff in the 40-60 percent streamflow duration range. Values for AGWETP, which control how much actual evapotranspiration can come from base flow, were set to zero to increase runoff during periods of low flow.

Two streamflow-gaging stations were used for calibrating streamflow, South River near Waynesboro (01626000) and South River at Harriston (01627500). These two streamflow-gaging stations are the only ones on the South River with complete daily streamflow data for the calibration period. Station 01626000 is the most upstream stream reach node in the model, whereas 01627500 is the penultimate downstream node.

Simulated streamflow exhibits annual, seasonal, and daily patterns similar to those in observed streamflow (figs. 24-31). Calibrated model simulation results compared to calibration goals are shown in tables 23 and 24 (Bicknell and others, 2001). There is a good overall mass balance for the simulation period and the distribution of high and low simulated flow matches well with observed values. The frequency distribution of simulated streamflow values matches the observed distribution, as shown by the flow duration curves in figures 32 and 33. High streamflows caused by storms, which occur infrequently but account for the majority of total discharge, show a close match between simulated and observed values. The lowest 20 percent of daily streamflows, from 80 percent to 100 percent exceedance in figures 32 and 33, are less accurately simulated, however, at Harriston, account for just 4.9 percent of total discharge volume.

**FIGURE 24 NEAR HERE**

**FIGURE 25 NEAR HERE**

**FIGURE 26 NEAR HERE**

**FIGURE 27 NEAR HERE**

Table 22. Primary model transport parameters changed from Chesapeake Bay Model Phase 5 values during calibration of the South River watershed model. [HSPF, Hydrologic Simulation Program-FORTRAN; ET, actual evapotranspiration; PERLND, pervious land area; IMPLND, impervious land area; RCHRES, model river reach]

| Type | HSPF Module | Parameter Name | Description |
|---|---|---|---|
| Hydrologic | | | |
| | PERLND | INFILT | controls infiltration capacity |
| | | ET coefficients | scale evaporation rate input time series |
| | | AGWETP | controls ET rate from base flow |
| Sediment Transport | | | |
| | IMPLND | loading factors | control fraction of sediment runoff from PERLND to RCHRES |
| | | KEIM | controls solids wash-off rate |
| | PERLND | loading factors | control fraction of sediment runoff from PERLND to RCHRES |
| | | NVSI | represents external application of detached soil |
| | | KRER | controls rate of soil detachment |
| | | KSER | controls rate of transport of detached soil |
| | RCHRES | W | particle settling velocity |
| | | TAUCD | critical bed shear stress for deposition |
| | | TAUCS | critical bed shear stress for scour |
| | | M | erodibility of bed sediment |

Table 23. Simulation results for the calibration period water years 1991 through 2000, calibrated model, South River, Virginia. [in., inches; %, percent]

| Runoff | Criterion | South River near Waynesboro 01626000 | | | South River at Harriston 01627500 | | |
|---|---|---|---|---|---|---|---|
| Category | (percent) | Observed (in.) | Simulated (in.) | %Error | Observed (in.) | Simulated (in.) | %Error |
| Total annual runoff | ±10 | 186.9 | 182.2 | -2.5% | 185.1 | 194.6 | 5.2% |
| Highest 10-percent flow | ±10 | 84.7 | 86.5 | 2.0% | 81.5 | 87.8 | 7.7% |
| Lowest 50-percent flow | ±15 | 28.0 | 25.6 | -8.4% | 31.5 | 31.4 | -0.2% |
| Winter runoff | ±15 | 64.3 | 61.6 | -4.3% | 63.0 | 64.7 | 2.6% |
| Spring runoff | ±15 | 65.9 | 63.4 | -3.9% | 63.6 | 66.5 | 4.5% |
| Summer runoff | ±15 | 26.1 | 26.7 | 2.2% | 26.2 | 29.7 | 13.4% |
| Fall runoff | ±15 | 30.8 | 30.5 | -1.1% | 32.2 | 33.7 | 4.7% |
| Total Storm Volume | ±20 | 19.6 | 17.1 | -13.0% | 19.0 | 17.4 | -8.5% |

Table 24. Simulation results for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River, Virginia. [in., inches; %, percent]

| Runoff Category | Criterion (percent) | South River near Waynesboro 01626000 Observed (in) | Simulated (in.) | %Error | South River at Harriston 01627500 Observed (in) | Simulated (in.) | %Error |
|---|---|---|---|---|---|---|---|
| Total annual runoff | ±10 | 35.5 | 32.5 | -8.6% | 35.3 | 34.9 | -1.0% |
| Highest 10-percent flow | ±10 | 14.0 | 13.2 | -5.5% | 13.8 | 13.4 | -2.8% |
| Lowest 50-percent flow | ±15 | 6.4 | 6.1 | -4.4% | 7.0 | 7.3 | 3.5% |
| Winter runoff | ±15 | 11.4 | 9.8 | -13.5% | 10.8 | 10.5 | -3.3% |
| Spring runoff | ±15 | 7.8 | 7.2 | -7.8% | 7.6 | 7.9 | 3.2% |
| Summer runoff | ±15 | 3.8 | 5.7 | 51.9% | 4.2 | 6.3 | 50.5% |
| Fall runoff | ±15 | 12.7 | 9.8 | -23.1% | 12.7 | 10.3 | -18.7% |
| Total Storm Volume | ±20 | 9.8 | 9.6 | -2.0% | 9.9 | 9.7 | -1.7% |

**FIGURE 28 NEAR HERE**

**FIGURE 29 NEAR HERE**

**FIGURE 30 NEAR HERE**

**FIGURE 31 NEAR HERE**

Observed daily-mean and simulated daily flows do not match in all cases, as can be seen in the 1:1 plots of observed to simulated streamflow, (figs. 34-35). The $R^2$ value for figure 34 is 0.39, and 0.41 for figure 35. The mismatch between daily values is, in many cases, caused by an offset in timing of a day or two between simulated and observed stormflows. The primary reason for differences between simulated and observed stormflows in most cases is probably differences between modeled and actual precipitation. As described in an earlier section, Meteorological and Climatic Data, the hourly precipitation data used in the South River watershed model were taken from the CBM5 model and were derived by spatial averaging of records from nearby meteorological monitoring stations, which for water years 1991 through 2000, were all outside the watershed. Although there are no hourly precipitation records from within the watershed during the calibration period, differences between actual precipitation on the basin and the precipitation time series in the model can be inferred from the fact that some observed storms had total storm discharge that exceed the model precipitation volumes for the same period. Similarly, some simulated storms have discharge volumes that exceeded observed precipitation volumes for the same period based on daily precipitation data collected within the watershed.

**FIGURE 32 NEAR HERE**

**FIGURE 33 NEAR HERE**

**FIGURE 34 NEAR HERE**

**FIGURE 35 NEAR HERE**

## Sediment Transport Model Calibration Results

The sediment transport component of the South River watershed model was calibrated using a "weight-of-evidence" approach (Donigian and Love, 2003), in which multiple numeric and qualitative calibration goals were assessed. Comparisons were made between simulated and observed suspended sediment concentration, suspended sediment loads, and depth of bed sediment. Comparisons were made using the same calibration period (water year 1991 through 2000), the same verification period (April 1, 2005, through March 31, 2007) and the same two calibration sites, (Waynesboro, 01626000, and Harriston 01627500), as were used for the calibration of streamflow. Only USGS suspended sediment concentration values were used for quantitative calibration of the sediment transport model. Suspended sediment values from the VDEQ (reported as total suspended solids as discussed earlier) were used only for qualitative and supplemental checks during the sediment model calibration.

Time series of regressed daily suspended sediment concentration values were used as the primary "observed" values during calibration because the regressed time series have values for every time step and therefore, their statistics are unbiased towards either stormflow or base flow. The regressed suspended sediment concentration time-series data were derived from USGS grab samples and multiple linear regression, as described earlier. So that a consistent regression model was used throughout the entire simulation period, regressed suspended sediment concentration values were used from estimation model number 7 in table 15, which derived suspended sediment concentration from normalized streamflow and streamflow increase. Observed suspended sediment loads were calculated by multiplying observed daily flow values with regressed suspended sediment concentration values, whereas simulated loads were calculated by HSPF using its mass balance formulas.

The South River watershed model has coarse spatial discretization relative to channel morphology and sediment distribution patterns. Riffle spacing in the South River is typically less than 0.2 mi, for example, (Pizzuto and others, 2006, page 24) whereas river reaches in the model are about 8.0 mi long. Due to the coarse discretization and the limited sediment transport algorithms available in HSPF, the accurate simulation of any single observed suspended sediment concentration value was not the primary focus of the calibration. Rather, the goal was to match simulated and observed suspended sediment concentration statistics and suspended sediment loads.

The multiple calibration goals were defined as follows:

1) Simulated suspended sediment concentration ranges match observed suspended sediment concentration ranges and simulated 50 percent and 10 percent duration suspended sediment concentration values are within 30 percent of observed values.
2) Simulated and observed suspended sediment concentration duration plots show no major differences.
3) Total simulated suspended sediment loads are within 10 percent of observed loads for the calibration period.
4) The total of the bottom 50 percent of daily simulated sediment loads and the top 10 percent of daily simulated sediment loads are within 30 percent of observed values.
5) Simulated annual sediment loads show patterns similar to observed annual loads.
6) Simulated depth of bed sediment does not show a long-term increasing trend.

Calibration goal 6 is based on the results of a study by Pizzuto and others (2006), who found that very little fine-grained sediment is stored on the channel bed of the South River, an amount that is "3 orders of magnitude less than the annual suspended sediment load of the South River, and is volumetrically insignificant." They found that average depth of sediment in the channel was less than 0.04 inches downstream of the plant site. On the basis of this observation, the model was calibrated so that depth of deposited sediment in each model river reach did not show long-term increasing trends. This goal was met in the calibrated model as shown in figure 36.

**FIGURE 36 NEAR HERE**

Selected sediment transport parameters for each impervious land area, pervious land area, and river reach were adjusted during the calibration process to obtain a better fit to observations (table 22). Changes to initial CBM5 parameter values were made to reduce the amount of sediment entering the river, to redistribute sediment loads across flow regimes, and to prevent sediment building up on the river bed. For impervious land areas, sediment transport coefficients KEIM were reduced by 50 percent. For pervious land areas, the coefficients NVSI, KRER, and KSER were reduced by 80 percent. For each impervious and pervious land area, coefficients used to adjust sediment loads reaching the river (sediment load factors) were reduced from CBM5 values (Gary Shenk, Chesapeake Bay Program, written commun., 2007; Chesapeake Bay Program, 2002, Appendix F) to achieve better sediment mass balance. Sediment load factors are multiplied into overland runoff sediment loads before they enter the river to improve mass balances. The calibrated South River watershed model uses the same sediment load factor value for all pervious and impervious land areas contributing to a reach. The load factor for reach 1 is 15.6 percent, reduced from the equivalent CBM5 value of 21 percent. For reaches 2-5, the load factor is 21 percent, reduced from the equivalent CBM5 value of 23 percent.

As can be seen in figures 37-44 and tables 25-26, the watershed model does a reasonable job of recreating observed grab samples, suspended sediment concentration ranges, and regressed concentrations and annual loads. The simulated annual sediment load at Harriston for the calibration period is 22,400 tons, of which 98 percent comes from pervious land area surfaces, 2 percent from impervious land area surfaces, and 0.1 percent from point-source discharges. Total simulated loads during the calibration period have an error of +2.1 percent at Harriston and -3.0 percent at Waynesboro, when compared to loads calculated from the regressed suspended sediment concentration time series. Yearly loads for Waynesboro and Harriston are shown in figures 41-44.

Time series of simulated and observed (regressed) suspended sediment concentration values are shown in figures 37 and 38 for the Waynesboro station and in figures 39 and 40 for the Harriston station. Simulated suspended sediment concentration values have an overall good match to observed values. All but one of the six numeric calibration goals was met (tables 25 and 26). The goal that was not met, the lowest 50 percent of suspended sediment concentration at the Waynesboro station, had -46.5 percent error due in part to simulated suspended sediment concentration being able to go to zero, whereas USGS grab sample data had a minimum suspended sediment value of 1.0.

**FIGURE 37 NEAR HERE**

**FIGURE 38 NEAR HERE**

**FIGURE 39 NEAR HERE**

**FIGURE 40 NEAR HERE**

Table 25. Comparison of simulated and observed (regressed) daily sediment concentrations and loads, calibration period water years 1991 through 2000, calibrated model, South River, Virginia. [mg/L, milligrams per liter; %, percent]

| | | Criterion | South River near Waynesboro (01626000) | | | South River at Harriston (01627500) | | |
|---|---|---|---|---|---|---|---|---|
| | | (percent ) | Observed (Regressed) | Simulated | % Error | Observed (Regressed) | Simulated | % Error |
| Suspended sediment concentration (mg/L) | 90th percentile | ±30% | 29.4 | 26.1 | -11.4% | 30.3 | 33.2 | 9.5% |
| | 50th percentile | ±30% | 6.6 | 6.5 | -1.2% | 6.8 | 7.5 | 9.7% |
| Sediment load (tons) | Total | ±10% | 125,500 | 125,000 | -0.2% | 231,700 | 224,300 | -3.2% |
| | Top 10 % | ±30% | 113,600 | 116,100 | 2.2% | 212,600 | 204,500 | -3.8% |
| | Lowest 50% | ±30% | 1,000 | 1,200 | 15.7% | 2,100 | 2,600 | 26.6% |

Table 26. Comparison of simulated and observed (regressed) daily sediment concentrations and loads, verification period April 1, 2005, through March 31, 2007, calibrated model, South River, Virginia. [mg/L, milligrams per liter; %, percent]

| | | Criterion | South River near Waynesboro (01626000) | | | South River at Harriston (01627500) | | |
|---|---|---|---|---|---|---|---|---|
| | | (percent ) | Observed (Regressed) | Simulated | % Error | Observed (Regressed) | Simulated | % Error |
| Suspended sediment concentration (mg/L) | 90th percentile | ±30% | 23.7 | 23.9 | 0.8% | 24.5 | 25.7 | 4.8% |
| | 50th percentile | ±30% | 7.8 | 4.1 | -46.5% | 7.6 | 5.5 | -28.5% |
| Sediment load (tons) | Total | ±10% | 19,100 | 18,100 | -5.5% | 29,900 | 32,800 | 9.8% |
| | Top 10 % | ±30% | 16,800 | 16.600 | -1.1% | 26,300 | 29,800 | 13.4% |
| | Lowest 50% | ±30% | 300 | 200 | -16.9% | 500 | 500 | -13.5% |

Simulated annual sediment loads have the same temporal pattern of change as observed (regressed) annual loads, but show less range of variation. The difference between simulated and observed (regressed) loads in 1996 is due primarily to a storm on January 19 that had a daily observed (regressed) load of 40,400 tons but a simulated load of only 1,600 tons (figs. 41 and 43). Streamflow also was undersimulated for this storm in both cases due to differences between modeled and actual precipitation. Similarly, the difference between simulated and observed (regressed) loads in 1998 occurred primarily during two February storms in which streamflow, and therefore sediment load, were undersimulated.

Sediment transport is dominated by infrequent high-flow events and individual storms can have a large effect on annual sediment loads.

The mean observed (regressed) annual sediment load from 1991 through 2000 at monitoring station 01627500 is 23,170 tons/yr (tons per year). This compares to an annual mean load calculated in the Pizzuto and others (2006) study of 10,100 tons at the same location for the period 1967 through 2003 using different estimation methods. Both the Pizzuto load estimate and the "observed" load estimate calculated for this study are subject to considerable uncertainty. The uncertainty in simulated loads results from uncertainty in the suspended sediment concentration regression, sampling errors propagating through the calibration, uncertainty in flow estimates, use of daily average rather than instantaneous flow values, and the inherent uncertainty of representing low frequency high load events based on periodic data and linear estimation methods.

**FIGURE 41 NEAR HERE**

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**FIGURE 44 NEAR HERE**

Sediment results for the calibrated model during the calibration and verification periods are shown in tables 25 and 26. Simulated loads are comparable to those reported in other studies of Chesapeake Bay watersheds. (Phillips, 2007; Langland and others, 2003)

Duration plots for simulated and observed (regressed) suspended sediment concentration are shown in figure 45 for the calibration period and in figure 46 for the verification period. Duration plots are comparable to cumulative distribution functions and express the percent of time that a variable (suspended sediment concentration in this case) exceeds a given value. The simulated and observed (regressed) suspended sediment concentration duration plots are visually similar at both the Waynesboro and Harriston monitoring stations.

**FIGURE 45 NEAR HERE**

**FIGURE 46 NEAR HERE**

## Mercury Transport Model Calibration Results

The mercury transport component of the South River watershed model was calibrated by adjusting parameters so that hourly simulated total mercury concentrations match observed concentrations in grab samples from the river. Unlike water and sediment, there are no continuous time series of observed mercury concentrations to use as a calibration goal. Calibration of mercury transport also differed from water and sediment in that it used a 1-year calibration period, from April 1, 2005, through March 31, 2006, and a 1-year verification period, from April 1, 2006, through March 31, 2007. Three monitoring sites were used for calibration -- 01626000 (Waynesboro), 01626920 (Dooms), and 01627500 (Harriston). As with sediment calibration, USGS mercury concentration data were used for quantitative comparison to simulated results and data from the VDEQ were used for additional visual checks.

Although the calibration process compared observed and simulated concentrations, these values have somewhat different characters. Hourly simulated concentrations represent average conditions in a river reach over a 1-hour period and do not capture variability occurring within a reach or at time intervals less than 1 hour. Observed THG concentration values represent instantaneous vertically averaged conditions at the centroid of flow at a single point along the river. In the actual river, there likely is substantial variation of THG concentrations within a reach and within an hour time span, therefore simulated concentrations are not expected to match observed concentrations exactly. Instead, the goal was to recreate observed THG statistics and spatial and temporal patterns.

Initial calibration efforts indicated that downstream of the plant site, the model had insufficient sources of mercury to the river during stormflow recession periods and during other times of declining streamflow when there was no surface runoff. This was true despite the fact that hydrology and sediment transport were well calibrated, incorporating all explicitly known mercury sources, and using assigned model input mercury concentrations that matched observed values. Results from an example simulation with sediment runoff mercury adjusted to match storm peak values are shown in figure 47. When mercury on runoff sediment was assigned unrealistically high concentrations, simulated THG values could be raised to match observed values at the low end, but then simulated high end values were much too high.

**FIGURE 47 NEAR HERE**

To calibrate the mercury model, an additional mercury source was added to the model to mimic channel margin inputs of mercury to the river, as discussed in the earlier section of this report describing the mercury transport model. Channel margin mercury loads are linked to ground-water discharge (AGWO) and interflow (IFWO), and therefore occur during low and moderate flow and during periods of no surface runoff. The coefficients multiplied into IFWO and AGWO time series were adjusted during calibration to match simulated to observed THG concentrations. No channel margin inputs were used for model river reach 1 because they were not needed to achieve good calibration, and because model river reach 1 is upstream of the historic mercury source.

Final calibrated concentrations for mercury sources to the river are shown in table 27. These concentrations are within the range of observed concentrations. Although there are no observations of interflow ($THG_F$), the calibrated value of 10.0 ng/L is reasonable because interflow is conceived as precipitation traveling through the shallow subsurface for a few days or less before discharging to the river. Therefore it is expected that interflow would have a $THG_F$ concentration between that of ground water and precipitation (0.07 ng/L and 21.8 ng/L), respectively.



Table 27. Input mercury concentrations to the calibrated watershed model. [$THG_F$, aqueous filterable total mercury; $THG_{SS}$, total mercury on solids suspended in water; ng/L, nanograms per liter; µg/g, milligrams per liter]

| Mercury Source and Hydrologic Response Unit Type | Calibrated Model Concentration Value |
|---|---|
| Ground water $THG_F$ concentrations (ng/L) | |
| Uncontaminated Pervious Land Areas | 0.7 |
| Contaminated Flood-plain Areas | 2.9 |
| Interflow $THG_F$ concentrations (ng/L) | |
| Uncontaminated Pervious Land Areas | 10.0 |
| Contaminated Flood-plain Areas | 10.0 to 16.7 |
| Precipitation $THG_F$ concentrations (ng/L) | 21.8 |
| Runoff Sediment Associated Mercury $THG_{SS}$ concentrations µg/g | |
| Uncontaminated Pervious Land Areas | 0.061 |
| Contaminated Flood-plain Areas | 7.6 to 16.7 |

With the channel margin inputs added to the model, it was possible to successfully calibrate the model to match observed THG concentrations in the river. The time series of calibrated THG values are shown in figures 48a-c for the Waynesboro, Dooms, and Harriston stations, respectively. For all three monitoring stations, the model produces reasonably accurate simulations of water column THG concentrations. Simulated THG concentrations from the calibrated model have a slightly wider range than observed concentrations, because grab samples are unlikely to capture the very highest and lowest concentrations. Simulated high concentrations during storm events agree well with observed storm sample concentrations in figures 48a-c.

Simulated mercury concentration values do not match all observed values, however. These discrepancies may result from a variety of factors including errors in the sediment or hydrologic components of the model, errors in mercury component input or parameterization, or real world variability at scales below the model discretization. During periods of extended low flow, when THG concentrations are low, the simulated hourly THG concentrations for both Waynesboro and Harriston (figs. 48a and 48c) exhibit spurious numerical oscillations. These oscillations have an hourly period driven by a corresponding oscillation in suspended sediment concentration. As a result of numerical dispersion and (or) rounding errors, the model at each hourly time step alternately deposits or resuspends a large percentage of the suspended sediment that is present in the water column. Most mercury in the water column is attached to sediment, and this causes the total water column mercury concentrations to oscillate as well. This is clearly a numerical artifact of the model simulation and was not observed in South River sample data. These oscillations do not affect the mass balance of total mercury at periods of a day or more, and do not significantly affect the TMDL calculations because the 1-hour oscillation period is much shorter than the 90-day averaging period used to determine the TMDL.

Statistics for simulated THG concentrations from the calibrated model and for USGS observed concentrations at the three primary South River monitoring stations are listed in table 28. Results for the calibration and verification periods have been combined to produce the statistics in table 28. Simulated mercury statistics closely approximate observed mercury statistics. Undersimulation of the 90$^{th}$-percentile THG concentration value at Waynesboro is at least partially the result of multiple storm samples being collected at that monitoring station in October and November 2005 (fig. 48a), causing bias in the sample population towards the high end. Similarly at Dooms, where a smaller percentage of storm samples were collected, the 90$^{th}$-percentile value is oversimulated (fig. 48b).

**FIGURE 48A NEAR HERE**

**FIGURE 48B NEAR HERE**

**FIGURE 48C NEAR HERE**

Table 28. Statistics for hourly simulated and observed total mercury concentrations, calibrated watershed model, South River, Virginia, calibration and verification periods combined, April 1, 2005, through March 31, 2007. [observed values from U.S. Geological Survey samples only; %, percent; ng/L, nanograms per liter; THG, total unfiltered mercury]

| THG concentration (ng/L) | Waynesboro (01626000) | | | Dooms (01626920) | | | Harriston (01627500) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Observed | Simulated | % Error | Observed | Simulated | % Error | Observed | Simulated | % Error |
| 90$^{th}$ percentile | 14.9 | 7.1 | -52% | 568.3 | 988.0 | 74% | 895.2 | 898.8 | 0.4% |
| 50$^{th}$ percentile | 1.3 | 1.2 | -9% | 103.6 | 69.6 | -33% | 115.0 | 91.4 | -21% |
| 10$^{th}$ percentile | 0.7 | 0.7 | -5% | 29.5 | 31.7 | 8% | 29.3 | 26.5 | -10% |

Duration plots for simulated and observed (USGS samples only) mercury concentrations are shown in figures 49a-c for the Waynesboro, Dooms, and Harriston stations. Curves for the simulated THG duration show a reasonable match to observed duration curves at all three monitoring stations.

**FIGURE 49A NEAR HERE**

**FIGURE 49B NEAR HERE**

**FIGURE 49C NEAR HERE**

Simulated mercury loads to the river are listed by source in table 29. Nonpoint sources account for 99.7 percent of the mercury load to the South River. The largest of the nonpoint sources are channel margin inputs, accounting for about 84 percent of all mercury entering the river. Runoff from land surfaces, primarily from contaminated flood-plain areas, accounts for most of the rest. Point sources, ground-water discharge, interflow discharge, and precipitation on the river surface collectively account for less than 1 percent of the mercury load to the South River.

Table 29. Simulated annual total mercury loads to the South River, calibrated model, existing conditions, April 1, 2005, through March 31, 2007. [%, percent]

| | Total Mercury (grams/year) | | | | | |
|---|---|---|---|---|---|---|
| Reach | 1 | 2 | 3 | 4 | 5 | Total all Reaches |
| Point Sources | 1 | 608 | 0 | 0 | 41 | 650 (0.3%) |
| Direct Precipitation to River | 28 | 7 | 2 | 11 | 8 | 55 (0.0%) |
| Interflow Discharge | 382 | 46 | 48 | 151 | 41 | 667 (0.4%) |
| Ground-Water Discharge | 54 | 8 | 7 | 24 | 6 | 99 (0.1%) |
| Runoff | 573 | 144 | 3,998 | 21,205 | 3,316 | 29,237 (15.4%) |
| Channel Margin Inputs | 0 | 59,179 | 82,742 | 14,551 | 2,241 | 158,713 (83.8%) |
| Totals | 1,038 (1%) | 59,992 (32%) | 86,797 (46%) | 35,942 (19%) | 5,653 (3%) | 189,421 (100%) |

# Limitations of the South River Watershed Model and Suggestions for Future Investigations

A number of factors limit the accuracy of the HSPF South River model simulations. A primary factor is the spatial and temporal discretization within the model, particularly spatial discretization. Parameters such as water velocity, sediment depth, suspended sediment concentration, and mercury concentration exhibit a wide range of values over relatively small distances (less than 100m) in the South River. The model treats all such variables as homogeneous within each river reach, however. Model reach lengths range from 1.5 to 24.6 mi. Temporal discretization is less of an issue because the model progresses in 1-hour time steps. During periods of flooding, however, and particularly at the beginning of a runoff event, hydrologic variations can be substantial from one hour to the next. There were not enough data to justify finer spatial discretization of the model. Collecting data at additional monitoring stations could provide the data needed for future calibration of the model at finer spatial scales.

A second limitation of the model is the exclusion of physical mechanisms that may be major controls on mercury transport. Although inputs of mercury from channel margin processes, such as bank collapse and erosion, make up more than 80 percent of the mercury load to the river in the calibrated model (table 29), these mercury inputs to the river are treated in the model as simple lumped parameter processes rather than explicit physical processes. Related to this limitation is the lack of data describing the magnitude and timing of these processes. Detailed studies of the timing and spatial extent of mercury release from channel margin sediments in response to changes in temperature, pH, and oxidative states could improve understanding of the channel margin mercury loading, for example. Ongoing studies are examining the effects of hyporehic flow and bank collapse on loading of mercury to the river. These and other future research efforts could improve the understanding of channel margin inputs of mercury and guide changes to the watershed model that could improve its accuracy and certainty in model output.

Deficiencies in model input data are an additional potential source of model error. Precipitation data are the primary hydrologic input to the model and have partially known errors, as previously discussed, that directly affect simulation results. Precipitation has spatial variation at scales smaller than the land-county segments used to assign precipitation time series. Additional precipitation data could reduce this uncertainty in the model. Because most observed mercury concentration values are high relative to background levels, model results are tied to relatively few calibration data at low concentrations. The model was designed to accurately simulate the full range of concentrations currently seen in the watershed, most of which are much greater than the TMDL target concentration of 3.8 ng/L. None of the samples collected downstream of the plant site in this study had THG concentrations below 13 ng/L. If more low concentration mercury data were available, perhaps after initial cleanup efforts, it could help reduce uncertainty associated with simulation of low mercury concentrations. This uncertainty is especially applicable to the TMDL Scenarios discussed later in this report, which examine potential clean-up efforts and their effects on THG concentrations in the river. Ground-water $THG_F$ data are sparse and the model value for $THG_F$ concentrations in ground water from contaminated pervious lands areas is assigned primarily on the basis of data from a single contaminated flood-plain area. Additional mercury concentration data for ground water would be useful for reducing uncertainty in future modeling efforts.

Limitations that should be noted by both readers and model users are that the HSPF model in its current state relies heavily on data collected since 2004, and that data related to mercury loading to the river prior to 2004 are relatively sparse and generally not produced by low-level detection laboratory methods for measuring mercury concentrations. Before 2004, there were several early reports on fish tissue concentrations and sediment and soil concentrations, but there were few reliable and low-detection mercury concentration data for plant outfalls or the South River. Mercury sources to the river and mercury concentrations within the river may have changed significantly over the past 30 years, but the model does not reflect those changes due to insufficient data. This limitation does not apply to dates from 2004-07, but should be considered if the model is used to simulate mercury transport during other time periods.

## Simulation of Mercury Total Maximum Daily Load (TMDL)

Subsequent to calibration of the mercury transport component of the watershed model, the model was used to simulate a TMDL for mercury in the South, South Fork Shenandoah, and Shenandoah Rivers. The TMDL value is set at a level to ensure that mercury loads from point sources and nonpoint sources can be assimilated without exceeding the criterion of 0.3 mg/kg methylmercury in fish tissue. Allocations from point sources, nonpoint sources, and natural background sources are included in the TMDL. The South River TMDL includes an implicit margin of safety to account for uncertainties in calculation of the TMDL. The South River was analyzed in detail and results were then extrapolated downstream to determine a TMDL for both the South Fork Shenandoah and Shenandoah Rivers.

## Designation of Endpoints

The South River model links the identified sources of mercury to water column concentrations of total mercury (THG). An empirical bioaccumulation model then relates THG concentrations to fish tissue concentrations. The watershed model, in conjunction with the bioaccumulation model, provides the basis for estimating the total assimilative capacity of the river and any needed load reductions (Virginia Department of Environmental Quality, 2008b). The mercury TMDL for the South River is then determined as a mercury loading rate that is consistent with the endpoint fish tissue methylmercury concentration of 0.3 mg/kg.

Numeric endpoint water column total mercury concentration values were determined by the VDEQ based on the 0.3 mg/kg fish tissue methylmercury level and the empirical bioaccumulation model (table 30). These target concentrations were used to evaluate attainment of acceptable water quality and represent water-quality goals that will be targeted through load-reduction scenarios. The target concentrations decrease downstream to account for variations in fish size and natural variability of bioaccumulation rates in the Shenandoah river system.

For each modeled river reach, simulated total mercury concentrations were compared to target concentrations to determine whether a violation had occurred. Simulated 90-day median THG concentrations were used in the comparison. On a daily basis, simulated 90-day median THG concentrations were compared to target concentrations for each river. If for that day, the median total mercury concentration for the preceding 90-day period was higher than the target concentration, then a violation had occurred.

## Existing Conditions

The calibrated South River watershed model was run with a simulation period of April 1, 2005, through March 31, 2007, to simulate existing conditions in the South River. When 90-day median THG concentrations are below target endpoint concentrations (table 30), fish are protected from tissue mercury concentrations above 0.3 mg/kg. If 90-day median THG concentrations exceed target concentrations then fish are expected to have tissue mercury concentrations in excess of 0.3 mg/kg. Table 31 shows median hourly total mercury concentrations for the entire period, April 1, 2005, through March 31, 2007 (730 days).

Table 30. Target total mercury water column concentrations for rivers in the study. [g, grams; ng/L, nanograms per liter; THG, total unfiltered mercury]

| Water Body | Normalized Fish Size (g) | Target Water Column THG Concentration (ng/L) |
|---|---|---|
| South River | 218 | 3.8 |
| South Fork Shenandoah River | 253 | 3.2 |
| Shenandoah River | 321 | 2.5 |

Table 31. Simulated total mercury concentrations for the South River, Virginia, existing conditions, median hourly concentrations for the period April 1, 2005, through March 31, 2007. [- indicates upstream; ng/L, nanograms per liter]

| Model River Reach | Reach End Node | Miles Downstream from Plant Site | THG Concentration (ng/L) Simulated median |
|---|---|---|---|
| 1 | 01626000 | -2.8 | 1.2 |
| 2 | 01626850 | 2.3 | 21.7 |
| 3 | 01626920 | 5.3 | 69.6 |
| 4 | 01627500 | 16.5 | 91.4 |
| 5 | Port Republic | 24.0 | 93.4 |

Under existing conditions, median mercury concentrations in the South River are below the target concentration of 3.8 ng/L only at the Waynesboro monitoring station, upstream of the plant site. Below the plant site, median THG concentrations exceed target concentrations by a factor of 5 or more (table 31). Rolling 90-day median THG simulated concentrations from the calibrated model under existing conditions are shown in figures 48 a-c. At the Waynesboro monitoring station, 90-day median THG concentrations are always below the target concentration of 3.8 ng/L, whereas, at Dooms and Harriston 90-day median THG concentrations are always far above it.

Simulated mercury loads in the South River under existing conditions are summarized in table 32. Mercury loads increase dramatically below the plant site (in reach 2) as a result of a variety of point and nonpoint source inputs. The annual mercury load of 189 kg/yr at Port Republic can be compared to the estimated 109 kg/yr of mercury loading due to bank retreat estimated by Rhoades and others (2009). Although the time period for the simulations (2005 through 2007) is shorter than the averaging period (1937 through 2006) used by Rhoades and others (2009), it is noteworthy that the two values are relatively close and the total simulated load is higher than the estimated load resulting solely from bank retreat.

Table 32. Simulated annual mercury loads by reach in the South River, existing conditions, April 1, 2005, through March 31, 2007. [- indicates upstream; USGS, U.S. Geological Survey; kg/yr, kilograms per year; mi, miles]

| Model River Reach | Endpoint | USGS Station ID | Distance Downstream from Plant Site (mi) | Total HG Load (kg/yr) |
|---|---|---|---|---|
| 1 | Waynesboro | 01626000 | -2.8 | 1.0 |
| 2 | Hopeman Parkway | 01626850 | 2.3 | 61.0 |
| 3 | Dooms | 01626920 | 5.3 | 147.8 |
| 4 | Harriston | 01627500 | 16.5 | 183.8 |
| 5 | Port Republic | None | 24 | 189.4 |

Table 33. Mercury loading rates to watersheds and sub-watersheds by model reach, calibrated model, existing conditions, South River, Virginia, April 1, 2005, through March 31, 2007. [g/yr, grams per year; g/acre/yr, grams per acre per year]

| | Model River Reach | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| Reach Subwatershed | | | | | |
| Subwatershed area, (acres) | 81,468 | 13,651 | 10,129 | 30,704 | 14,525 |
| Reach-specific mercury loading rate, (g/yr) | 1,038 | 59,992 | 86,797 | 35,942 | 5,653 |
| Reach-specific unit mercury loading rate, (g/acre/yr) | 0.013 | 4.395 | 8.569 | 1.171 | 0.389 |
| Total Upstream Watershed | | | | | |
| Total Upstream Area (acres) | 81,468 | 95,119 | 105,248 | 135,952 | 150,477 |
| Total watershed HG loading rate, (g/yr) | 1,038 | 61,030 | 147,827 | 183,768 | 189,421 |

The results indicate that, as expected, mercury loads to the river increase dramatically in model river reach 2, which contains the plant site. Mercury attributable to releases from the plant site, including legacy mercury entering the river through channel margin inputs and contaminated runoff sediment, increases the total load of mercury to the river by a factor of more than 100 when compared to background conditions. The relative percentage of different mercury loads also changes, as shown in figure 50. Upstream of the plant site, most mercury is loaded to the river through interflow or runoff of sediment at background $THG_{Sed}$ concentrations, whereas downstream of the plant site, channel margin inputs dominate mercury loads.

**FIGURE 50 NEAR HERE**

## Scenarios for Mercury Load Reductions

Simulated loads to the river were modified to determine how water column THG concentrations would respond. Mercury loads were increased or decreased to simulate possible future scenarios, as shown in table 34. Scenario 1, “existing conditions,” is discussed in the previous section.

Table 34. Mercury load-reduction simulation scenarios. [$THG_F$, aqueous filterable mercury; ng/L, nanograms per liter]

<table>
<tr><th>Type</th><th>Scenario</th><th colspan="2">Changes to mercury loading</th></tr>
<tr><td>Existing conditions</td><td>1</td><td colspan="2">All current mercury loads included</td></tr>
<tr><td>Future conditions</td><td>2</td><td>Point sources increased to maximum permitted discharge, outfall 011 added, precipitation and interflow concentrations reduced.</td><td rowspan="6">Precip, interflow, and spring flow $THG_F$ concentrations reduced</td></tr>
<tr><td rowspan="3">Single source reductions</td><td>3A</td><td>Point sources reduced to target stream concentrations.</td></tr>
<tr><td>3B</td><td>Channel margin inputs eliminated, point sources at max permitted.</td></tr>
<tr><td>3C</td><td>Runoff cleaned up to background conditions, point sources at max permitted.</td></tr>
<tr><td rowspan="2">Multiple source reductions</td><td>4A</td><td>Channel margin loads eliminated and runoff cleaned to background conditions, point sources at max permitted.</td></tr>
<tr><td>4B</td><td>Additionally reduce point sources to 3.8 ng/L.</td></tr>
</table>

## Future Conditions

Under Scenario 2, future conditions are simulated by increasing permitted point-source flows to limits set by current (2007) discharge permits. These “future conditions” are comparable to “build-out” scenarios used in other TMDL studies (Interstate Commission on the Potomac River Basin, 2004). Flow rates are increased to maximum permitted values but concentrations of mercury are not changed, reflecting that current permits do not specify maximum concentrations. Under future conditions, Invista outfall 011 is assumed to discharge directly to the South River under monthly average flow rates. Since 2002, flow from outfall 011 has actually been routed through the Invista wastewater treatment plant, but under the current discharge permit, it is allowed to flow directly to the river. It is also assumed that $THG_F$ concentrations in precipitation will decline by 19 percent (from 21.8 to 17.6 ng/L) as a result of USEPA’s Clean Air Interstate Rule and the Clean Air Mercury Rule (Alex Barron, Virginia Department of Environmental Quality, written commun., 2008), and that interflow $THG_F$ concentrations will therefore also decrease by 19 percent. These changes to point-source loads, atmospheric mercury deposition rates, and interflow mercury concentrations are included in Scenarios 2 through 4B.

The results of Scenario 2 show that “future conditions” cause higher median THG concentrations in all South River reaches, with the highest increase of 43 percent just below the plant site at Hopeman Parkway (table 35). These increases are due to the higher loads from Invista outfall 011 and the somewhat higher mercury loads from point sources that come with the assumption that maximum permitted flows are in effect. Simulated total mercury loads decrease slightly at the Waynesboro monitoring station and increase slightly at Hopeman Parkway (table 36). Mercury loads can decrease even though median mercury concentrations increase because loads are dominated by high flow periods whereas median concentrations are dominated by low flow periods. The violation of target concentrations in reaches 2-5 does not change under "future conditions." Simulated THG concentrations under future conditions at the Harriston monitoring station are shown in figure 51.

**FIGURE 51 NEAR HERE**

## Single Source Reductions

Sources of mercury to the South River were reduced one at a time to determine the resulting changes in river mercury concentrations. Under Scenario 3A, point-source loads are lowered by setting point-source THG concentrations to the target THG concentration of 3.8 ng/L, while keeping flow rates at the maximum permitted rates used in the "future conditions" of Scenario 2. All point-source mercury concentrations are set to 3.8 ng/L in Scenario 3A. The only other change to mercury source loads under Scenario 3A, as compared to the existing conditions of Scenario 1, is the reduction of atmospheric mercury deposition and interflow $THG_F$ concentrations as previously described. A comparison of the simulated THG values at the Harriston station (01627500) from Scenario 3A with those of Scenario 2 shows that reducing point source inputs lowers THG concentrations during low-flow periods (figs. 51-52). The results in table 36 indicate that point sources make a relatively small contribution to total loads. THG loads decrease by 6 percent at Waynesboro and decrease by less than 1 percent at reaches 2-5 downstream of the plant site. Point sources make a relatively larger contribution to median THG concentrations because median concentrations are more sensitive than loads to low THG concentrations (tables 35-36). Upstream of the plant site at Waynesboro, median concentrations increase by 7 percent, as they do under Scenario 2, and downstream of the plant site in reaches 2-5, median concentrations decrease from 9-14 percent. Simulated THG concentrations for Scenario 3A at Harriston are shown in figure 52.

**FIGURE 52 NEAR HERE**

Under Scenario 3B, channel margin mercury loads are eliminated, simulating the potential future effects of remediation strategies focused on streambanks. Reduction of atmospheric mercury deposition and interflow $THG_F$ concentrations to reflect expected future changes are also included. Point sources are restored to future conditions. The results of Scenario 3B show large declines in both mercury loads and concentrations downstream of the plant site (fig. 53 and tables 35-37). THG loads decline by 84 percent to 97 percent and median THG concentrations decline from 51 percent to 86 percent in reaches 2-5 downstream of the plant site. Despite the large THG concentration declines, all downstream monitoring stations are still in violation of target concentrations 100 percent of the time. Simulated THG concentrations for Scenario 3B at Harriston are shown in figure 53.

**FIGURE 53 NEAR HERE**

Under Scenario 3C, mercury contaminated sediment runoff is cleaned to background conditions to simulate a hypothetical future remediation of South River flood plains. $THG_{Sed}$ concentrations on sediment from contaminated flood-plain areas are reduced to $THG_{Sed}$ concentrations of uncontaminated land areas. Reductions of atmospheric mercury deposition and interflow $THG_F$ concentrations are again included. Point sources and channel margin inputs are restored to future conditions. Simulated THG concentrations from

Scenario 3C at the Harriston monitoring station are shown in figure 54. With mercury contaminated runoff cleaned up, THG loads decrease from 0.1 percent to 14.8 percent at monitoring stations downstream of the plant site. Median THG concentrations under this scenario increase relative to existing conditions because point sources are assumed to have maximum permitted flows, which particularly increases mercury loads to the river during base-flow periods. Median THG concentrations increase by 43 percent at Hopeman Parkway, 9 percent at Dooms, and 1 percent at Harriston. All monitoring stations downstream from the plant site remain in violation of target THG values under this scenario.

**FIGURE 54 NEAR HERE**

Table 35. Changes in median simulated total mercury concentrations, relative to existing conditions, April 1, 2005, through March 31, 2007, South River, Virginia. [%, percent]

| Model Scenario | Waynesboro (01626000) | Hopeman Pkwy (01626850) | Dooms (01626920) | Harriston (01627500) | Port Republic |
|---|---|---|---|---|---|
| 1 | ----------------- | Existing conditions | | | ----------------- |
| 2 | 7% | 43% | 13% | 4% | 2% |
| 3A | 7% | -14% | -11% | -9% | -10% |
| 3B | 7% | -51% | -77% | -85% | -86% |
| 3C | 7% | 43% | 9% | 1% | 0% |
| 4A | 7% | -52% | -78% | -87% | -88% |
| 4B | 34% | -94% | -97% | 10-97% | -98% |

Table 36. Percentage change to in-stream total mercury loads, relative to existing conditions, April 1, 2005, through March 31, 2007, South River, Virginia. [%, percent]

| Model Scenario | Waynesboro (01626000) | Hopeman Parkway (01626850) | Dooms (01626920) | Harriston (01627500) | Port Republic |
|---|---|---|---|---|---|
| 1 | ----------------- | | Existing conditions | | ----------------- |
| 2 | -5.7% | 0.1% | 0.0% | 0.0% | 0.0% |
| 3A | -5.9% | -0.9% | -0.4% | -0.3% | -0.3% |
| 3B | -5.7% | -96.9% | -96.0% | -85.1% | -83.8% |
| 3C | -7.2% | -0.1% | -2.7% | -13.5% | -14.8% |
| 4A | -7.2% | -97.0% | -98.7% | -98.7% | -98.6% |
| 4B | -5.6% | -99.6% | -99.9% | -99.7% | -99.9% |

Table 37. Percent of time that simulated 90-day median total mercury concentrations exceed the 3.8 nanogram per liter target concentration, April 1, 2005, through March 31, 2007, South River, Virginia. [%, percent]

| Model Scenario | Waynesboro (01626000) | Hopeman Parkway (01626850) | Dooms (01626920) | Harriston (01627500) | Port Republic |
|---|---|---|---|---|---|
| 1 | 0% | 100% | 100% | 100% | 100% |
| 2 | 0% | 100% | 100% | 100% | 100% |
| 3A | 0% | 100% | 100% | 100% | 100% |
| 3B | 0% | 100% | 100% | 100% | 100% |
| 3C | 0% | 100% | 100% | 100% | 100% |
| 4A | 0% | 100% | 100% | 100% | 100% |
| 4B | 0% | 0% | 0% | 0% | 0% |

## Multiple Source Reductions and Total Maximum Daily Load (TMDL) Scenario

The results of Scenarios 3A- 3C demonstrate that THG concentrations cannot be brought below target concentrations unless channel margin mercury loads are drastically reduced and other loads are also reduced. Under Scenario 4A, multiple loads are reduced; channel margin loads are totally eliminated and sediment runoff concentrations, $THG_{Sed}$, are reduced to background levels. Together, these two sources account for 99.2 percent of total mercury loads to the river (table 29). Precipitation and interflow are again reduced to reflect future reductions in atmospheric mercury deposition. The remaining mercury loads are from point sources, ground water, and background mercury levels in precipitation, interflow, runoff, and precipitation. Results from Scenario 4A indicate that in spite of greatly reduced mercury loads, violations of THG target concentrations still occur at all of the monitoring stations downstream of the plant site, as shown in figure 55 for the Harriston monitoring station.

**FIGURE 55 NEAR HERE**

Under Scenario 4B, mercury loads to the river are further reduced, resulting in mercury concentrations that meet TMDL requirements. Mercury loads from channel margin inputs and surface runoff are again reduced and a further load reduction is made by lowering all point sources to the target THG concentration of 3.8 ng/L. Because this scenario will be used for load allocation under TMDL regulations by the VDEQ, all point sources are assigned a fixed concentration of 3.8 ng/L, including the Stuart's Draft wastewater plant and Genicom, which under existing conditions have THG concentrations below 3.8 ng/L. Results show that 90-day median THG concentrations stay below 3.8 ng/L in all river reaches, as shown in figure 56 for the Harriston monitoring station.

**FIGURE 56 NEAR HERE**

TMDL requirements are satisfied under Scenario 4B and the TMDL for mercury to the South River above its confluence with the South Fork Shenandoah at Port Republic is 2.0 kg/yr (table 38). This value is reasonable from a mass balance point of view, considering the low target concentrations. As an example, if the target concentration of 3.8 ng/L is multiplied by the simulated annual volume of water passing Port

Republic, 2.7x10[11] L, the result is 1.0 kg of mercury, which is less than the TMDL value of 2.0 kg/yr. The TMDL value of 2.0 kg/yr is higher because the 90-day median statistic reduces the importance of stormflows, which carry most of the mercury load.

Table 38. Annual mercury loads under Total Maximum Daily Load (TMDL) conditions (Scenario 4B), South River, Virginia.

| | Total Mercury Load (grams) | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | Total all Reaches |
| Point Sources | 21.0 | 72.9 | 1.1 | 0.0 | 16.8 | 112 |
| Direct Precipitation to River | 22.6 | 5.7 | 1.3 | 8.9 | 6.4 | 45 |
| Interflow Discharge | 309.2 | 50.6 | 39.2 | 124.8 | 33.8 | 558 |
| Ground-Water Discharge | 53.9 | 7.8 | 7.5 | 23.9 | 5.7 | 99 |
| Runoff | 572.8 | 96.7 | 87.0 | 354.1 | 105.0 | 1,216 |
| Channel Margin Inputs | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0 |
| Reach Loads | 980 | 234 | 136 | 512 | 168 | 2,029 |
| Watershed Loads | 980 | 1,213 | 1,349 | 1,861 | 2,029 | 2,029 |

There are several reasons for the large percentage reduction in mercury loads required to achieve target in-stream THG concentrations. The first is that THG concentrations of inputs to the river are very high relative to the target concentration of 3.8 ng/L. Precipitation $THG_F$ is about 5 times higher than target THG concentrations, interflow $THG_F$ from uncontaminated land occupying most of the watershed is about 3 times higher than target THG concentrations, and some point-source THG concentrations are two to three orders of magnitude higher than target THG concentrations. That smallmouth bass at the background reference station upstream of the plant site had average mercury concentrations of 0.24 mg/kg from 1999-2007 also indicates that the mercury concentrations must be reduced to near background levels to achieve the fish tissue mercury concentration goal of 0.3 mg/kg.

Results of the simulations indicate that large percentage reductions in multiple mercury loads to the river would be required to lower fish tissue methylmercury concentrations to below the 0.3 mg/kg criterion. Although the largest contributing load in the simulations is from channel margin inputs, other loads that would need to be addressed include runoff from contaminated flood plains and point-source discharges. Due to the large reductions needed (over 99 percent of the total mercury load) achieving the goal of maintaining fish tissue methylmercury concentrations below 0.3 mg/kg in the South River will be challenging.

## Sensitivity of Total Maximum Daily Load (TMDL) Results to Model Parameter Values

The sensitivity of model results to input parameter values was assessed by altering parameter values and measuring the resulting changes to simulated mercury concentrations. Model sensitivity was assessed both under existing conditions and TMDL conditions (Scenarios 1 and 4B). Input parameters selected for the sensitivity analysis were those expected to have the greatest control over simulated THG concentrations (table 39). Most of the parameters analyzed have multiple values in the calibrated model because of variation by HRU or by time period. For the sensitivity analysis, changes were made to all values of a parameter on a percentage basis of ±50 percent. When precipitation was decreased by 50 percent, for example, all daily precipitation values for all HRUs were decreased by 50 percent. Instream mercury loads are reported to the tenth of a kilogram. Because thousands of input values go into the simulation of annual mercury loads , the appropriate number of significant figures for reporting model results cannot be formally computed. For the purposes of this report, the numbers have been rounded as much as possible, while still showing the differences among locations and runs.

Under the existing conditions scenario (Scenario 1), sensitivity was measured as the change in simulated median THG concentration at the Harriston monitoring station for the period April 1, 2005, through March 31, 2007. Results of the sensitivity analysis under existing conditions are shown in table 40.

Under the TMDL Scenario, sensitivity was measured as the change in the percent of time that 90-day rolling median THG concentrations at Harriston exceeded the 3.8 ng/L target concentration (table 41).

Table 39. Model input parameters changed during sensitivity analysis. [HSPF, Hydrologic Simulation Program-FORTRAN]

| Type | HSPF Module | Name | Description | Original Values |
|---|---|---|---|---|
| Hydrology | EXT SOURCES | Precipitation | Precipitation rates (inches per year) | 39 – 43 |
| Sediment | PERLND>SEDMNT>DETACH | KRER | Sediment detachment rate coefficient | 0.02 - 4.0 |
| | PERLND>SEDMNT>SOSED1 | KSER | Sediment runoff transport coefficient | 0.1 - 20.0 |
| | RCHRES>SEDTRN (Silt and Clay only) | W | Settling velocity | 0.0035 - 0.03 |
| | | TAUCD | Critical shear stress - Deposition | 0.6 |
| | | TAUCS | Critical shear stress - Suspension | 0.02 - 0.15 |
| | | M | Erodibility of bed sediment | 0.03 - 0.07 |
| Mercury sorption in river | RCHRES>GQUAL>ADSEDS | KD | Adsorption coefficient | 1 |
| | | ADRATE | Mercury phase transfer rate coefficient | 25 |

Results of the sensitivity analysis under existing conditions (table 41) show that median THG concentrations are most sensitive to parameters affecting suspension and deposition of sediment in the river during low-flow periods (TAUCD, TAUCS, and W). Under the TMDL Scenario, violation of the 3.8 ng/L target THG concentration is affected most by KRER, the sediment detachment rate, and TAUCD, the critical shear stress for deposition of suspended sediment. THG concentrations are most sensitive, under both existing conditions and TMDL conditions, to parameters controlling suspended sediment in the river because most mercury in the river is attached to suspended sediment. Sensitivities do not appear particularly high in this analysis, as ±50 percent changes to parameter values cause at most a ±24 percent change in THG concentrations and ±4 percent change in time that 90-day median concentrations exceed 3.8 ng/L. However, because the model treats channel margin loads very simply, this sensitivity analysis does not express the full uncertainty associated with the channel margin mercury loads. Future investigations that improve conceptual understanding and computer simulation of processes controlling the channel margin inputs have the potential to provide that needed aspect of the sensitivity analysis.

Table 40. Results of sensitivity analysis for existing conditions, changes to median concentrations for the period April 1, 2005, through March 31, 2007, South River at Harriston, Virginia (U.S. Geological Survey station no. 01627500). [HSPF, Hydrologic Simulation Program-FORTRAN; THG, total unfiltered mercury; ng/L, nanograms per liter]

| Parameter | | | | | Median THG (ng/L) | | |
|---|---|---|---|---|---|---|---|
| Type | HSPF Module | Name | Description | Original Values | -50% | Existing Conditions | +50% |
| Hydrology | EXT SOURCES | Precipitation | Precipitation rates | 39-43 inches per year | 92.3 | 91.4 | 91.1 |
| Sediment | PERLND> SEDMNT> DETACH | KRER | Sediment detachment rate coefficient | 0.02 - 4.0 | 79.0 | 91.4 | 96.1 |
| | PERLND> SEDMNT> SOSED1 | KSER | Sediment runoff transport coefficient | 0.1 - 20.0 | 80.5 | 91.4 | 96.9 |
| | RCHRES> SEDTRN (Silt and Clay only) | W | Settling velocity | 0.0035 - 0.03 | 78.8 | 91.4 | 108.7 |
| | | TAUCD | Critical shear stress - Deposition | 0.6 | 76.0 | 91.4 | 98.3 |
| | | TAUCS | Critical shear stress - Suspension | 0.02 - 0.15 | 95.6 | 91.4 | 71.1 |
| | | M | Erodibility of bed sediment | 0.03 - 0.07 | 101.1 | 91.4 | 79.7 |
| Mercury sorption in river | RCHRES> GQUAL> ADSEDS | KD | Adsorption coefficient | 1 | 89.7 | 91.4 | 92.1 |
| | | ADRATE | Mercury phase transfer rate coefficient | 25 | 89.5 | 91.4 | 92.3 |

Table 41. Results of sensitivity analysis under the Total Maximum Daily Load (TMDL) Scenario, changes to percent of time that 90-day median concentrations exceed the 3.8 ng/L target concentration, South River at Harriston, VA (U.S. Geological survey station no. 01627500), April 1, 2005, through March 31, 2005. [%, percent]

| | | | % Time in Violation | | |
|---|---|---|---|---|---|
| | Name | Description | -50% | Scenario 4B | +50% |
| Hydrology | Precipitation | Precipitation rates (inches per year) | 0% | 0% | 0% |
| Sediment | KRER | Sediment detachment rate coefficient | 0% | 0% | 3.9% |
| | KSER | Sediment runoff transport coefficient | 0% | 0% | 0% |
| | W | Settling velocity | 0% | 0% | 0% |
| | TAUCD | Critical shear stress – Deposition | 0% | 0% | 2.5% |
| | TAUCS | Critical shear stress – Suspension | 0% | 0% | 0% |
| | M | Erodibility of bed sediment | 0% | 0% | 0% |
| Sorption | KD | Adsorption coefficient | 0% | 0% | 0% |
| | ADRATE | HG phase transfer rate coefficient | 0% | 0% | 0% |

# Implications for the Downstream South Fork Shenandoah River and Shenandoah River

The South Fork Shenandoah River and Shenandoah River are also part of the mercury TMDL, and are discussed here in light of the South River modeling results. Monitoring data were not collected in the South Fork Shenandoah and Shenandoah Rivers specifically for this study, but the VDEQ regularly collects surface-water samples for THG analysis at sites along the South Fork Shenandoah River. The most downstream site with sufficient mercury data for comparison to the South River is the South Fork Shenandoah River near Luray, Virginia (01629500) (fig. 57).

Twenty-seven data pairs of THG concentration values from the VDEQ were used to compare THG concentrations in the South Fork Shenandoah River to those in the South River. The analysis compared THG concentrations from the South River at Harriston (01627500) to those from the South Fork Shenandoah near Luray, Virginia (01629500), which were collected within 6 hours of each other between August 2001 and January 2007. The 1:1 plot of these values (fig. 57) has an $r^2$ value of 0.81, indicating a strong positive correlation. Instantaneous THG loads at sample times were estimated by multiplying THG concentrations by streamflow. THG loads were smaller at Luray than upstream in the South River at Harriston, with 22 of 27 sampling events showing a downstream decrease in load and an average decrease of 25 percent. This is in spite of the fact that the South Fork Shenandoah River near Luray receives drainage from the South River and from other tributary streams, most notably the Middle and North Rivers.

**FIGURE 57 NEAR HERE**

A possible explanation for the decrease in mercury load at the Luray monitoring station is that mercury from the South River may be sorbing to suspended solids in the South Fork Shenandoah and being deposited on the channel bed. Although sediment-deposition characteristics of the South Fork Shenandoah are not well known, long-term accumulation of large volumes of sediment seems unlikely for that reach.

For this TMDL, mercury concentrations in the South Fork Shenandoah near Luray were estimated from a mixing model of South River water and water at background THG concentrations from other tributaries to the South Fork Shenandoah. It is assumed that all mercury exiting the South River remains in the water column and moves downstream to the South Fork Shenandoah. Based on the ratio of annual streamflow for the South Fork Shenandoah River near Luray to annual streamflow for the South River at Port Republic from the HSPF model (4.96), it is estimated that 79.9 percent of the flow at Luray originates from outside the South River watershed. All water entering the South Fork Shenandoah River above Luray from uncontaminated sub-watersheds is assumed to have background THG concentrations equal to 1.81 ng/L, the mean for observed THG concentrations (VDEQ samples only) in the North River. THG concentrations for the South Fork Shenandoah near Luray were then estimated as a mix of South River mercury and background aqueous mercury. This estimation was made for existing conditions (Scenario 1) and for the TMDL Scenario (Scenario 4B). Resulting time series are shown in figure 58 relative to the 3.2 ng/L target concentration for the South Fork Shenandoah River.

The results shown in figure 58 indicate that 90-day median THG concentrations in the South Fork Shenandoah River under existing conditions exceed the 3.2 ng/L target concentration. Under the TMDL Scenario (4B), in which runoff, channel margin inputs, and point sources are cleaned up, 90-day median concentrations stay below the target concentration of 3.2 ng/L and therefore, no violations occur. The mercury load originating from areas other than the South River is estimated at 1.8 kg/yr, based on Luray flow volume minus South River Flow volume times the background mean THG concentration of 1.8 ng/L in the North River. The mercury TMDL for the South Fork Shenandoah River near Luray is therefore 3.8 kg/yr, obtained by adding 1.8 kg/yr to the South River mercury TMDL. By use of the same methods, a mercury TMDL of 4.1 kg/yr is estimated for the South Fork Shenandoah at Front Royal, Virginia (01631000), just upstream from the confluence with the North Fork Shenandoah River.

**FIGURE 58 NEAR HERE**

The Shenandoah River, formed at the confluence of the North Fork and South Fork Shenandoah Rivers in Front Royal, Virginia, also requires a mercury TMDL. Therefore, a TMDL was estimated using the same methods as those used for the South Fork Shenandoah River. However, there are few mercury data available for the Shenandoah River and there is no streamflow-gaging station in the affected part of the river, from Front Royal downstream to the Craig Run confluence. Annual average flow for the Shenandoah River at Craig Run is 2,791 $ft^3/s$, based on the USGS EDNA calculator (http://edna.usgs.gov/), which calculates drainage areas from digital elevation models and flow accumulation regression methods (Vogel and others, 1999; and http://edna.usgs.gov/). The South River occupies 9.8 percent of the drainage area and is assumed to provide 9.8 percent of flow in the Shenandoah River at the confluence with Craig Run. The remaining 90.2 percent of flow is assumed to originate from uncontaminated parts of the watershed that contribute water at background mercury concentrations. By again assuming that water from uncontaminated sub-watersheds has a background THG concentration of 1.81 ng/L, THG concentrations were estimated on a daily basis for the Shenandoah River at the confluence with Craig Run (fig. 59). The TMDL for mercury in the Shenandoah River at the Craig Run confluence, calculated as the sum of mercury from the South River plus mercury from uncontaminated sub-watersheds, is 6.1 kg/yr (table 42)

**FIGURE 59 NEAR HERE**

Table 42. Estimated total maximum daily loads (TMDLs) for mercury for listed waters in the Shenandoah Valley, Virginia. [THG, total unfiltered mercury; ng/L, nanograms per liter; kg/yr, kilograms per year]

| River | Target THG Concentration (ng/L) | Total Mercury TMDL (kg/yr) |
|---|---|---|
| South River at Port Republic, Virginia | 3.8 | 2.0 |
| South Fork Shenandoah River near Luray, Virginia | 3.2 | 3.8 |
| South Fork Shenandoah River at Front Royal, Virginia | 3.2 | 4.1 |
| Shenandoah River at Craig Run, Virginia | 2.5 | 6.1 |

# Summary

The U.S. Geological Survey (USGS), in cooperation with the Virginia Department of Environmental Quality and the U.S. Environmental Protection Agency, conducted a study to develop a total maximum daily load (TMDL) for methylmercury in fish tissue in the South, South Fork Shenandoah, and Shenandoah Rivers

of Virginia. These rivers have fish with methylmercury concentrations above the U.S. Environmental Protection Agency criterion of 0.3 mg/kg (milligrams methylmercury per kilogram of fish tissue). A numerical watershed model based on Hydrological Simulation Program–FORTRAN (HSPF) software was developed to simulate water, sediment, and mercury transport in the South River watershed. This model was calibrated with field data collected in this study. Data were also compiled from other studies to describe other media including fish tissue and to expand coverage of downstream rivers and time periods prior to 2005. On the basis of results from the calibrated watershed model, the mercury load to the South River under existing conditions for the period April 2005 through March 2007 was 189 kilograms per year. Using a site-specific empirical bioaccumulation model, the Virginia Department of Environmental Quality calculated concentrations of methylmercury in fish tissue from water column concentrations of total mercury. On the basis of the bioaccumulation model, to reduce fish tissue methylmercury concentrations below the U.S. Environmental Protection Agency criterion of 0.3 mg/kg, water column concentrations of total mercury need to be below target concentrations of 3.8 ng/L (nanograms per liter) in the South River, 3.2 ng/L in the South Fork Shenandoah River, and 2.5 ng/L in the Shenandoah River. Reductions in mercury loads to the South River were simulated using the calibrated HSPF model to determine the source-load reductions required to meet these conditions. Simulation results indicate that the TMDL for mercury in the South River that would be protective of methylmercury in fish tissue is 2.0 kilograms of total mercury per year. A mixing model and conservative mercury transport based on the South River modeling results were used to calculate mercury TMDLs for the South Fork Shenandoah and Shenandoah Rivers, which were 4.1 and 6.1 kilograms of mercury per year, respectively. Under the assumptions used in this study, if mercury loads to the South River are reduced so that fish tissue methylmercury concentrations are brought below

0.3 mg/kg, fish tissue methylmercury concentrations in the South Fork Shenandoah River and Shenandoah River will also be reduced to less than 0.3 mg/kg.

Major findings and conclusions of this study are:

- The calibrated South River watershed model simulates observed characteristics of streamflow, sediment load, and mercury transport.
- Analysis of mercury loads to the South River indicates that nonpoint-source loads account for over 99 percent of total loads under existing conditions.
- Channel margin mercury load, a nonpoint-source load, makes up an estimated 84 percent of total mercury load to the South River. The channel margin mercury loads originate from contaminated sediment in close proximity to the river, but the pathways and mechanism(s) responsible for moving the channel margin mercury to the river are not well understood.
- A 99 percent or greater reduction in the current mercury load delivered to the South River is required to meet target water-column mercury concentrations that are protective of the U.S. Environmental Protection Agency 0.3 mg/kg criterion for methylmercury in fish tissue.
- The mercury TMDL is estimated to be 2.0 kg/yr for the South River at Port Republic, 4.1 kg/yr for the South Fork Shenandoah River at Front Royal, and 6.1 kg/yr for the Shenandoah River at the Craig Run confluence.



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# Appendix 1- Data Sources Used to Define Point-Source Loading in the Model

**Appendix 1.** Data sources used to define point-source loading.

[cfs, cubic feet per second; mg, milligrams; NPDES, National Pollutant Discharge Elimination System; %, percent; FPBS, Frew Pond Baker Spring; TSS, total suspended solids; SSC suspended sediment concentration; Hg, mercury; ng/L, nanograms per liter; THG, total unfiltered mercury; mg/L, milligrams per liter; conc., concentration; GW, groundwater; K, hydraulic conductivity; Disch., discharge]

| Point sources | | Discharge (cfs) | | | Suspended solids concentration (TSS or SSC), mg/L | | | Total unfiltered Hg concentration (THG), ng/L | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Name | Model ID | Data source and type | Model value assignment: Periods with data | Model value assignment: Periods of no data | Data source and type | Model value assignment: Periods with data | Model value assignment: Periods of no data | Data source and type | Model value assignment: Periods with data | Model value assignment: Periods of no data |
| Stu Draft STP | 101-103 | NPDES monthly 2001-2007 | monthly observed values | Average monthly | NPDES monthly 2001-2007 | monthly observed values | Average monthly | periodic samples, n=1 | – | THG = 0.7 ng/L |
| Loth Spring | 201-203 | None | – | Estimate = 25% of FPBS | None | – | Use FPBS average TSS = 9 mg/L | None | – | Use FPBS avg. THG = 4.1 ng/L |
| INVISTA Outfalls | | Invista, DuPont, NPDES | | | Invista, DuPont, NPDES | | | DuPont, DEQ | | |
| 001 | 211-213 | daily 1998-2007 | daily observed values | Average monthly | periodic samples, n=45 | – | Base flow TSS average = 2.6 mg/L Stormflow TSS average = 3.4 mg/L | periodic samples, n=41 | – | Regression on Flow |
| 003 | 231-233 | periodic measurements | – | Regression on daily river flow | periodic samples, n=31 | – | Base flow TSS average = 4.5 mg/L Stormflow TSS average = 8.9 mg/L. | periodic samples, n=40 | – | Base flow THG avg. = 41.2 Ng/L Stormflow THG avg. = 61.6 ng/L |
| 004 | 241-243 | periodic measurements | – | Regression on daily river flow | periodic samples, n=13 | – | Base flow TSS average = 1.1 mg/L. Stormflow TSS average = 25.7 mg/L. | periodic samples, n=8 | – | Base flow THG avg = 15.5 Ng/L Stormflow THG avg = 42.1 ng/L |
| 006 | | Ignored based on insignificant contribution | | | Ignored based on insignificant contribution | | | Ignored based on insignificant contribution | | |
| 008 | 281-283 | periodic measurements | – | Regression on daily river flow | periodic samples, n=26 | – | Base flow TSS average = 6.3 mg/L, Stormflow TSS average = 32 mg/L | periodic samples, n=31 | – | Base flow THG avg. = 298.4 Ng/L Stormflow THG avg. = 134.9 ng/L |
| 009 | 291-293 | periodic measurements | – | Base flow = 0 Stormflow simulated by HSPF | periodic samples, n=4 | – | No Base flow, Stormflow average TSS = 7.2 mg/L | periodic samples, n=4 | – | No Base flow, Stormflow avg. THG = 81.9 ng/L |
| 010 | 221-223 | periodic measurements | – | Base flow = 0 Stormflow simulated by HSPF | periodic samples, n=3 | – | No Base flow, Stormflow average TSS = 46.8 mg/L | periodic samples, n=4 | – | No Base flow, Stormflow avg. THG = 228.4 ng/L |
| 011 | 271-273 | Daily 1998-2002 and overflow event monitoring 2005-2006 | daily observed values | Average monthly | periodic samples, n=28 | – | Base flow TSS average = 24.5 mg/L, Stormflow TSS average = 20.3 mg/L | periodic samples, n=37 | – | Base flow THG avg. = 2278 ng/L Stormflow THG avg. = 393 ng/L |
| 012 | 274-276 | None | | Base flow = 0 Stormflow simulated by HSPF | None | – | set = 010 conc. at given time and flow | None | – | set = 010 conc. at given time and flow |

**Appendix 1.** Data sources used to define point-source loading.—Continued

[cfs, cubic feet per second; mg, milligrams; NPDES, National Pollutant Discharge Elimination System; %, percent; FPBS, Frew Pond Baker Spring; TSS, total suspended solids; SSC suspended sediment concentration; Hg, mercury; ng/L, nanograms per liter; THG, total unfiltered mercury; mg/L, milligrams per liter; conc., concentration; GW, groundwater; K, hydraulic conductivity; Disch., discharge]

| Point sources | | Discharge (cfs) | | | Suspended solids concentration (TSS or SSC), mg/L | | | Total unfiltered Hg concentration (THG), ng/L | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Name | Model ID | Data source and type | Model value assignment: Periods with data | Model value assignment: Periods of no data | Data source and type | Model value assignment: Periods with data | Model value assignment: Periods of no data | Data source and type | Model value assignment: Periods with data | Model value assignment: Periods of no data |
| 013 | 277-279 | Overflow event monitoring | Individual overflow events | Average annual volume | None | – | set = 001 conc. for stormflow events | None | – | set = 001 conc. for stormflow events |
| 014 | 224-226 | Overflow event monitoring | Individual overflow events | Average annual volume | None | – | set = 001 conc. for stormflow events | None | – | set = 001 conc. for stormflow events |
| FPBS | 204-206 | periodic monitoring | – | Average plus seasonal variation of ± 29% | periodic samples, n=3 | – | Average TSS = 9 mg/L | periodic samples, n=3 | – | avg. THG = 4.1 ng/L |
| GW Disch. | 207-209 | Darcian flux gw levels (7 wells), slug test K (5 wells) | – | Average flux | None | – | Assume TSS = 0 | periodic samples, n=32 | – | avg. THG = 6.9 ng/L |
| Wboro STP | 261-263 | NPDES monthly 2001-2007 | monthly observed values | Average monthly | NPDES monthly 2001-2007 | monthly observed values | Average monthly values | periodic samples, n=1 | – | THG = 7.6 ng/L |
| Genicom | 301-303 | NPDES monthly 2001-2007 | monthly observed values | Average monthly | None | – | Assume TSS = 0 | periodic samples, n=1 | – | THG = 0.2 ng/L |
| Alcoa | 501-503 | NPDES monthly 2001-2007 | monthly observed values | Average monthly | NPDES monthly 2001-2007 | monthly observed values | Average monthly values | periodic samples, n=1 | – | THG = 18.3 ng/L |

# Appendix 2 - User's Control Input File for the Calibrated South River Watershed Model Under Existing Conditions.

Appendix 2 will be included in digital form in the final published report .

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*http://va.water.usgs.gov*

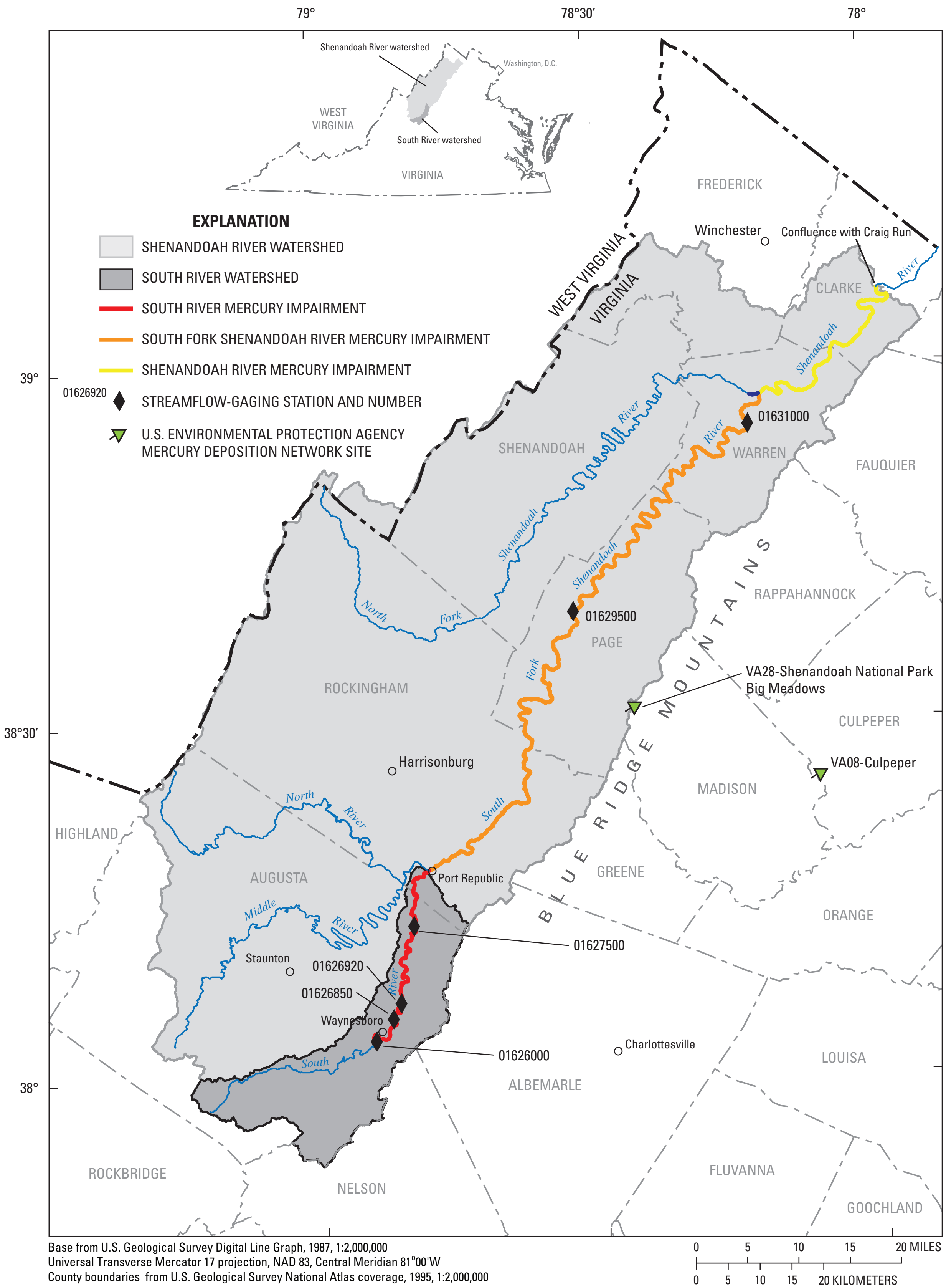



**Figure 1.** Location of rivers in the Shenandoah Valley, Virginia, on the 303d list of contaminated water for elevated concentrations of methylmercury in fish tissue.

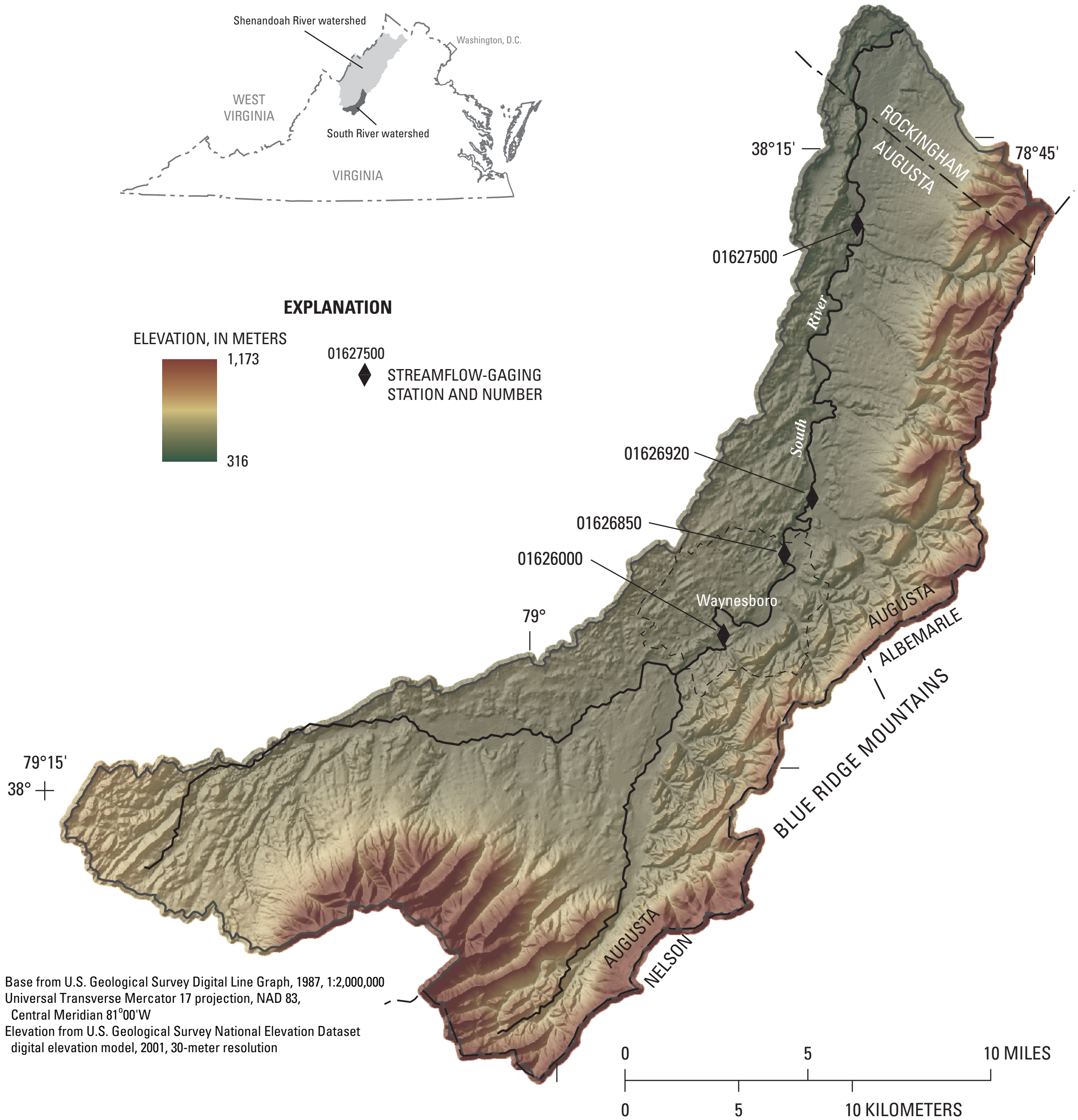



**Figure 2.** Location of the South River watershed study area in the Shenandoah Valley, Virginia.

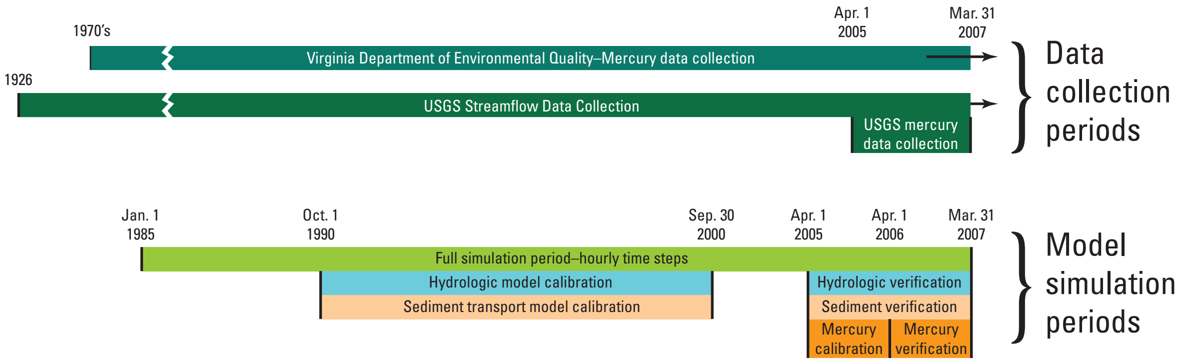



**Figure 3.** Timeline for data collection and model simulation, South River, Virginia.

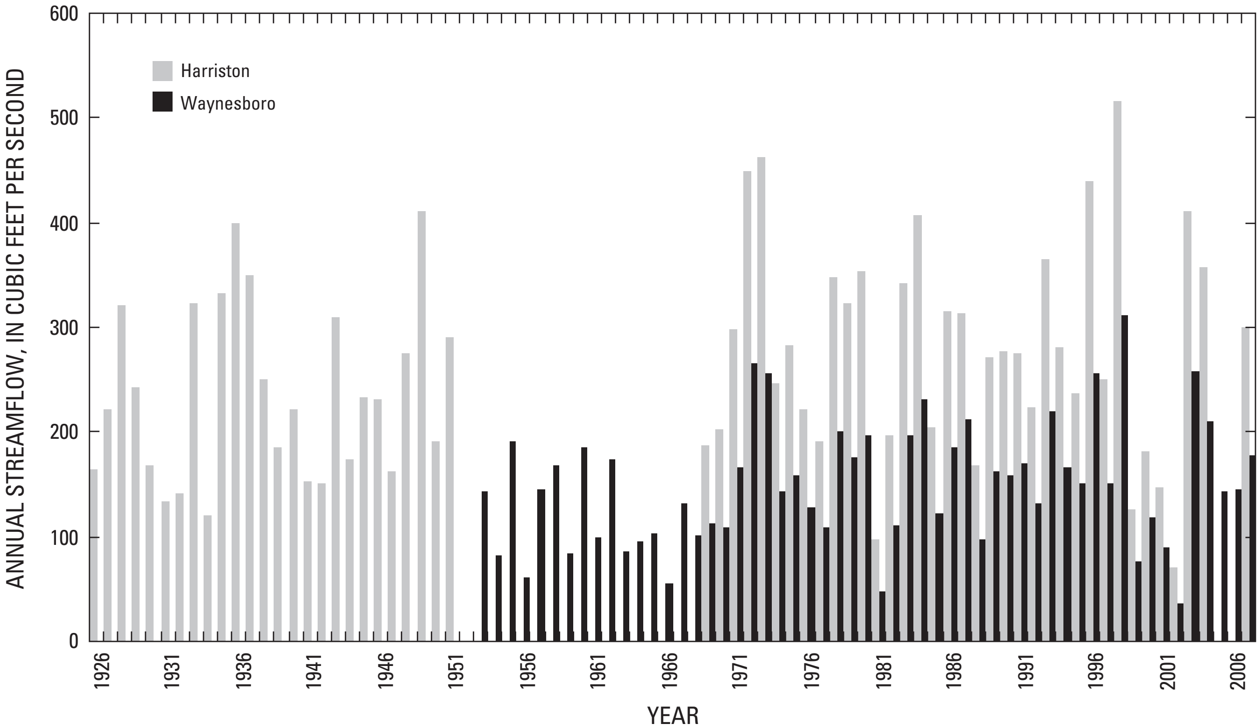



**Figure 4.** Annual streamflow for the South River near Waynesboro (USGS station number 01626000) and at Harriston (USGS station number 01627500), Virginia, water years 1926-2007.

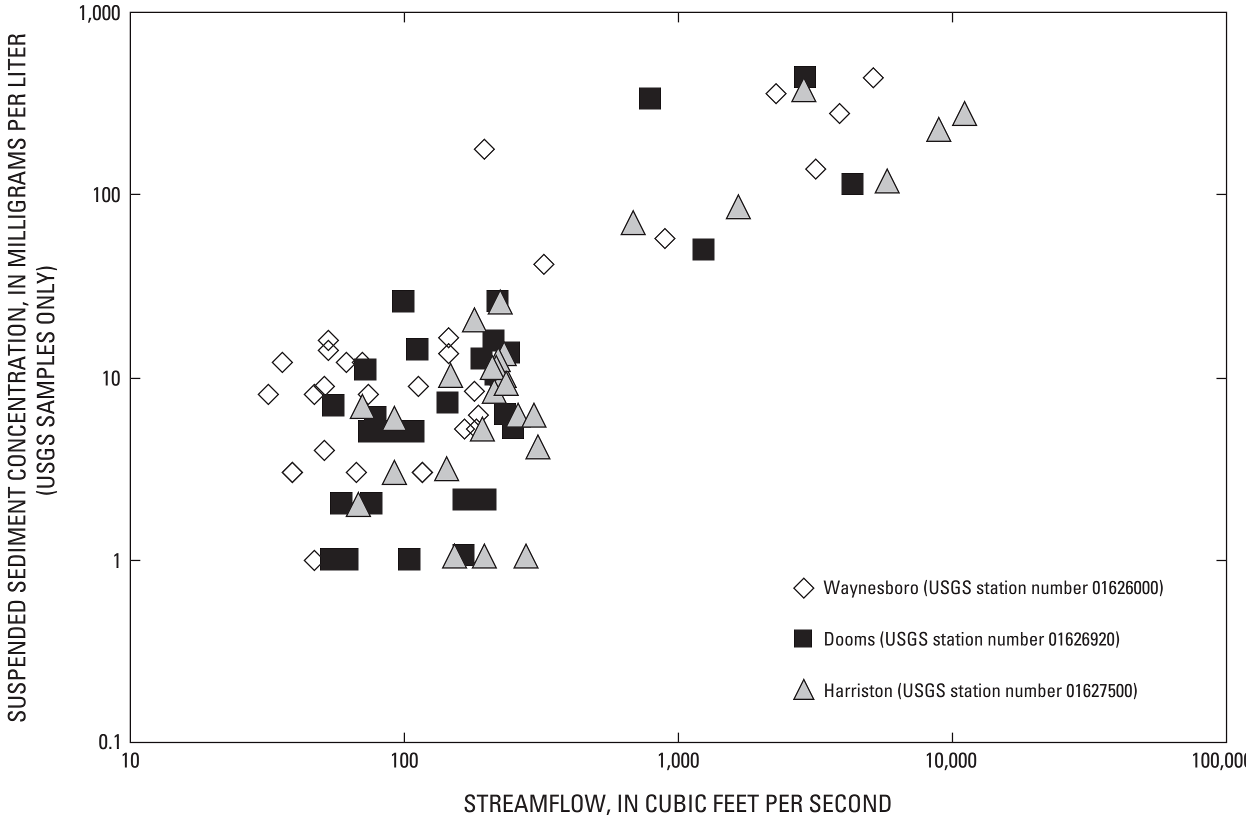



**Figure 5.** Observed suspended sediment concentrations and streamflow in the South River, Virginia, April 1, 2005, through March 31, 2007.

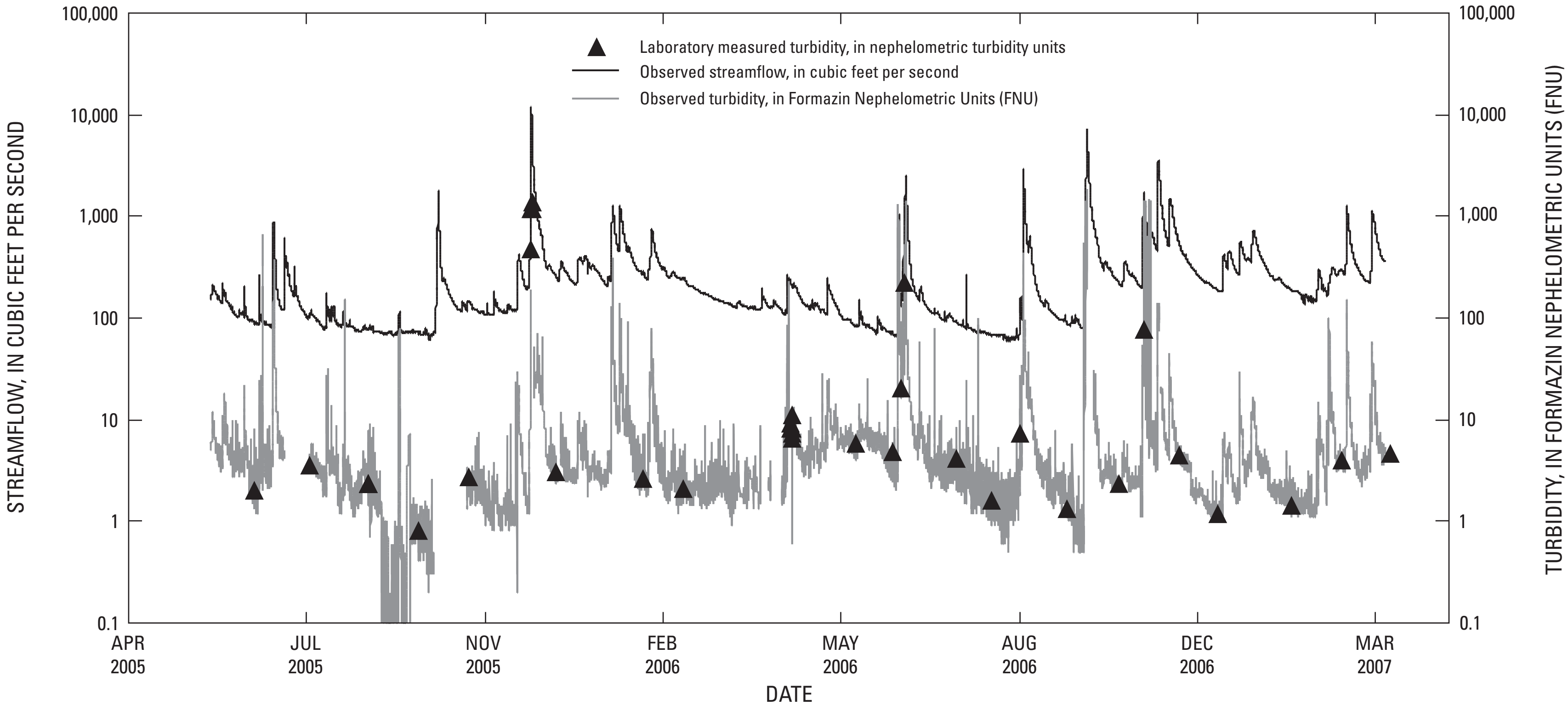



**Figure 6.** Streamflow and turbidity from June 2005 through April 2007 for the South River at Harriston (USGS station no. 01627500), Virginia. [Data recorded at 15-minute intervals.]

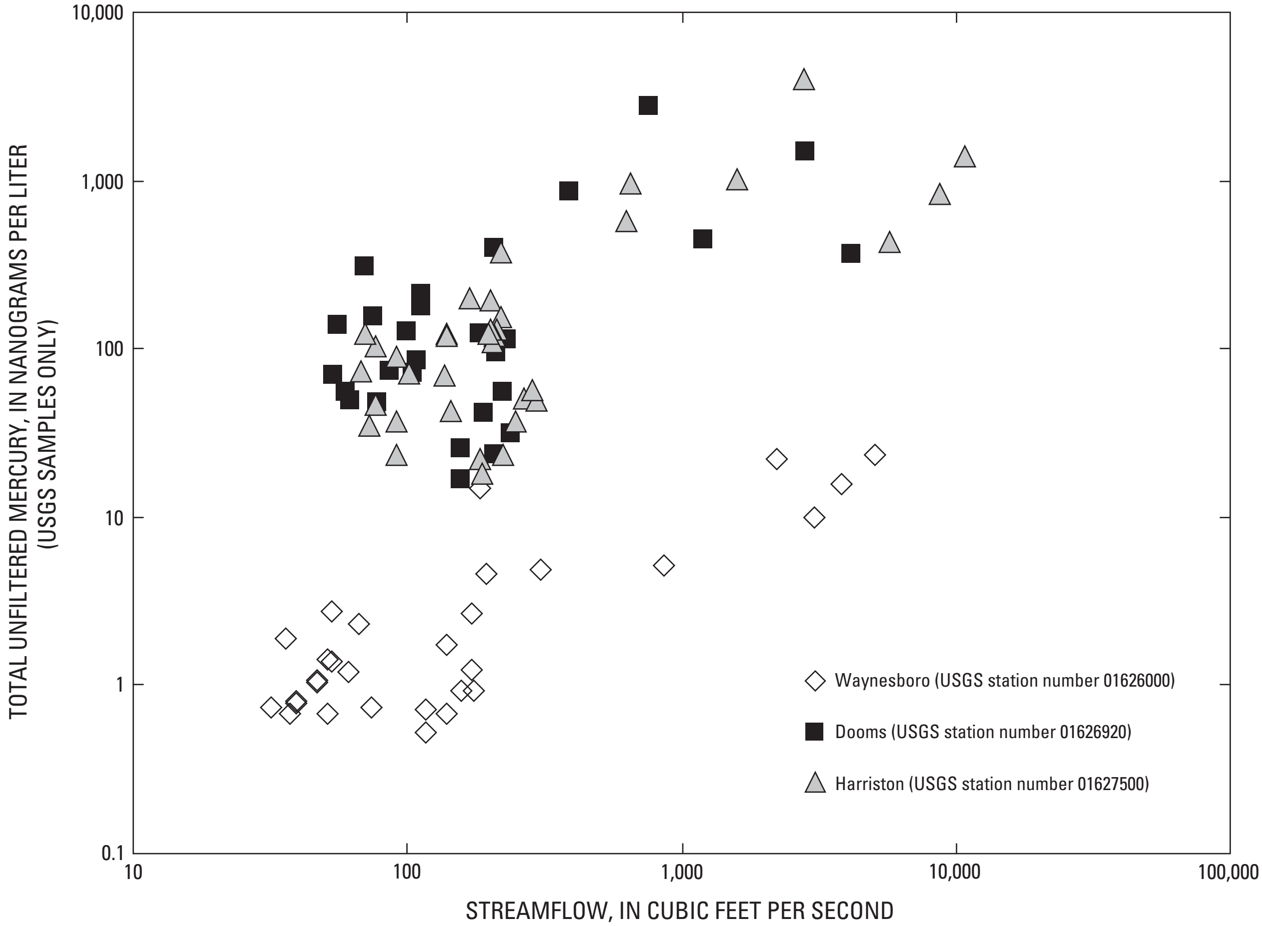



**Figure 7.** Observed total unfiltered mercury concentration and concurrent instantaneous streamflow in the South River, Virginia, April 1, 2005, through March 31, 2007.

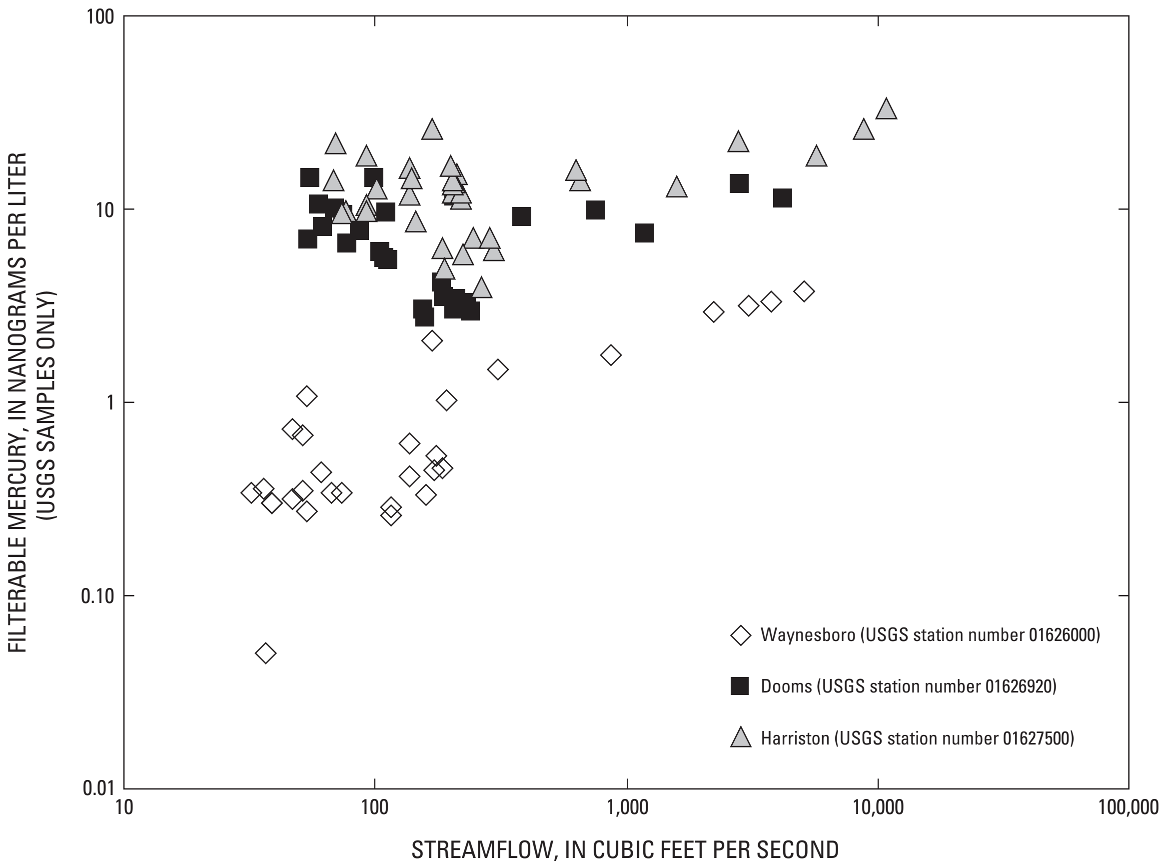



**Figure 8.** Observed aqueous concentration of filterable mercury and concurrent instantaneous streamflow, South River, Virginia, April 1, 2005, through March 31, 2007.

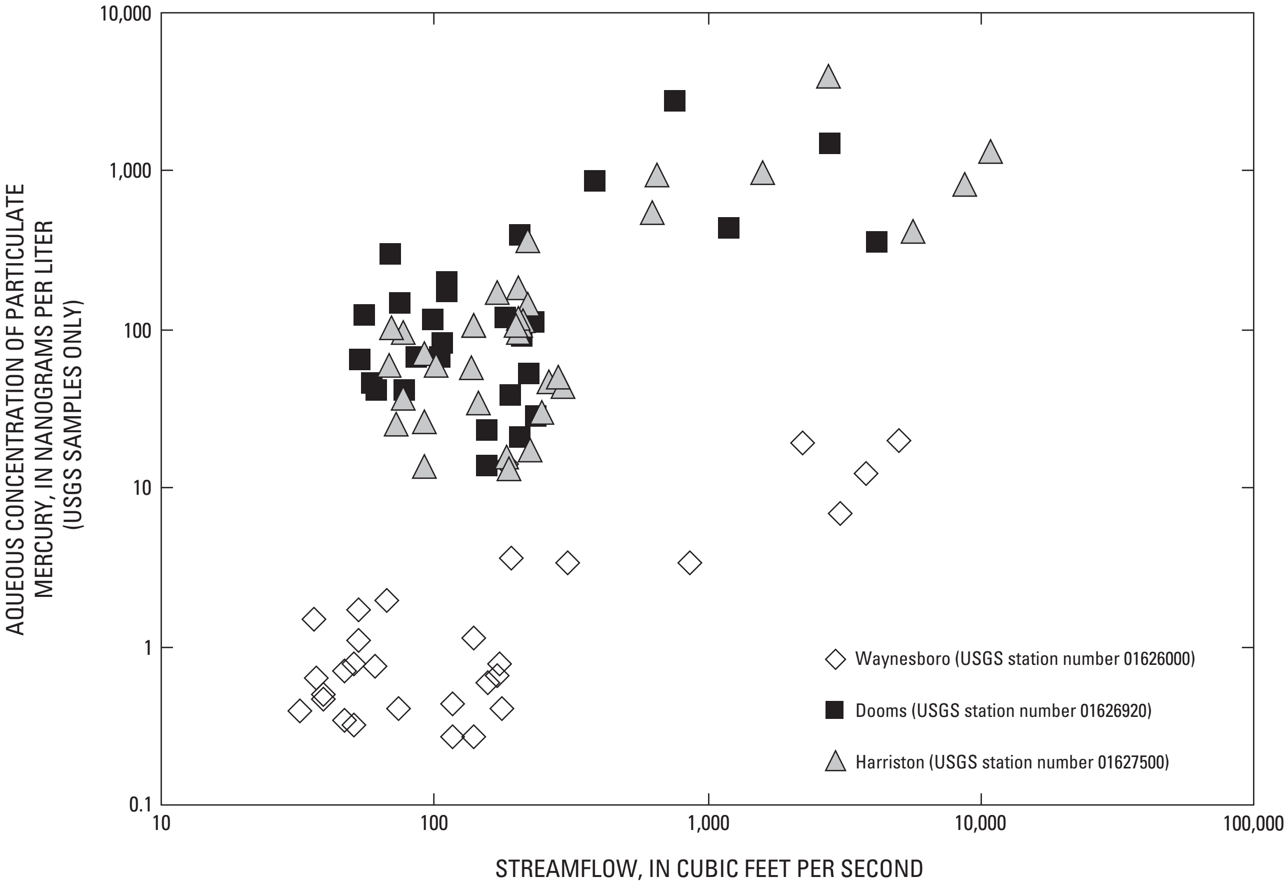



**Figure 9.** Observed aqueous concentration of mercury associated with particulate matter and concurrent instantaneous streamflow, South River, Virginia, April 1, 2005, through March 31, 2007.

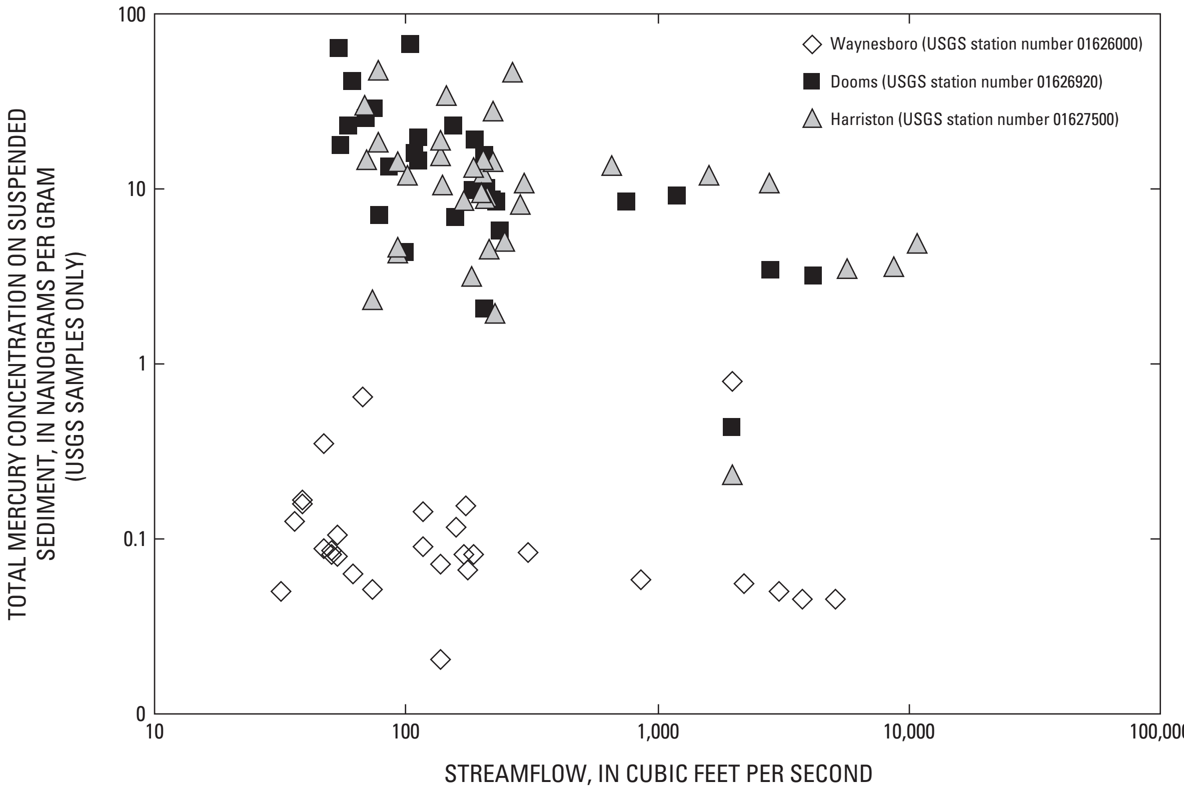



**Figure 10.** Observed concentration of mercury on suspended particulate matter and concurrent instantaneous streamflow, South River, Virginia, April 1, 2005, through March 31, 2007.

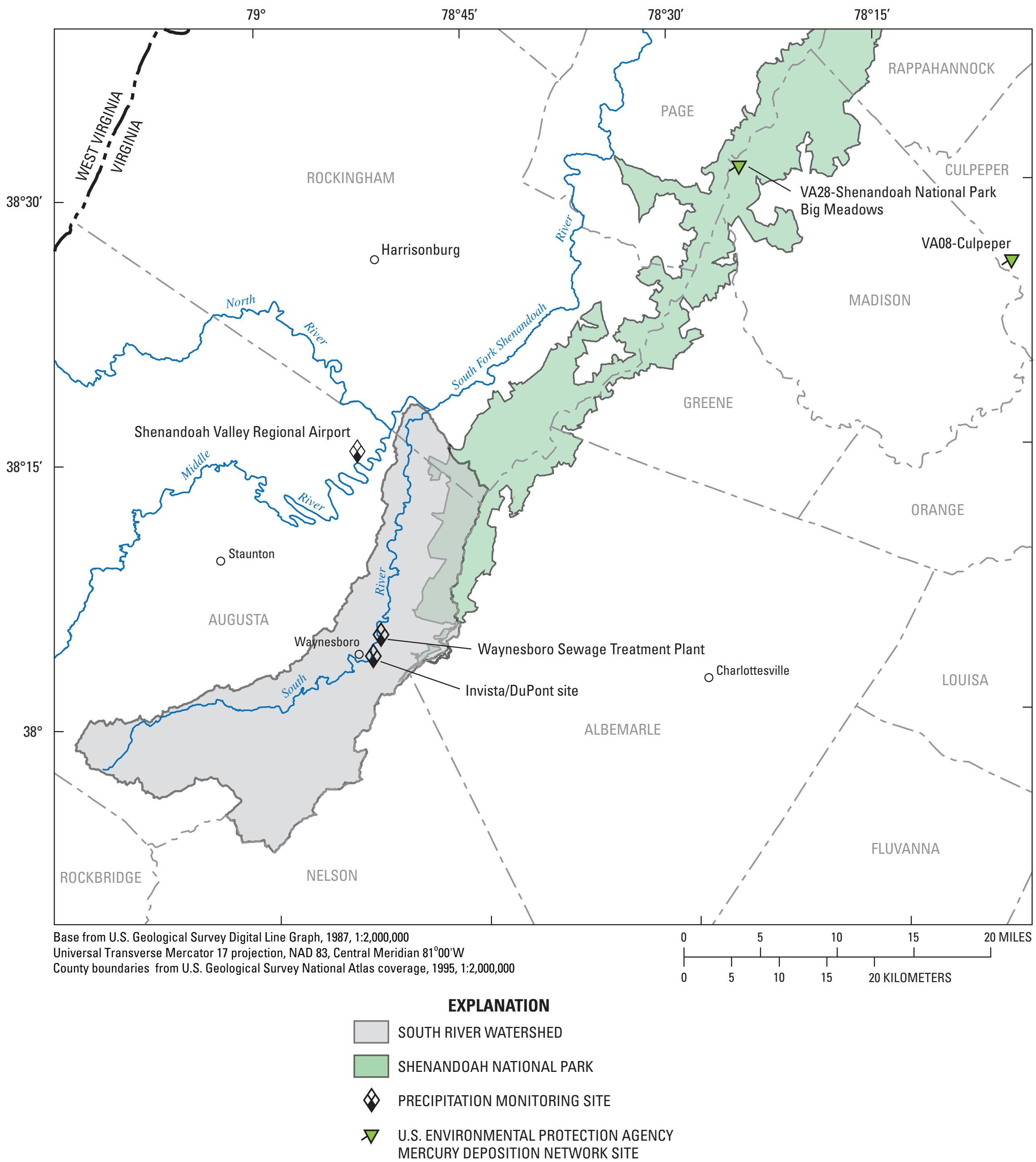



**Figure 11.** Location of mercury deposition and precipitation monitoring sites.

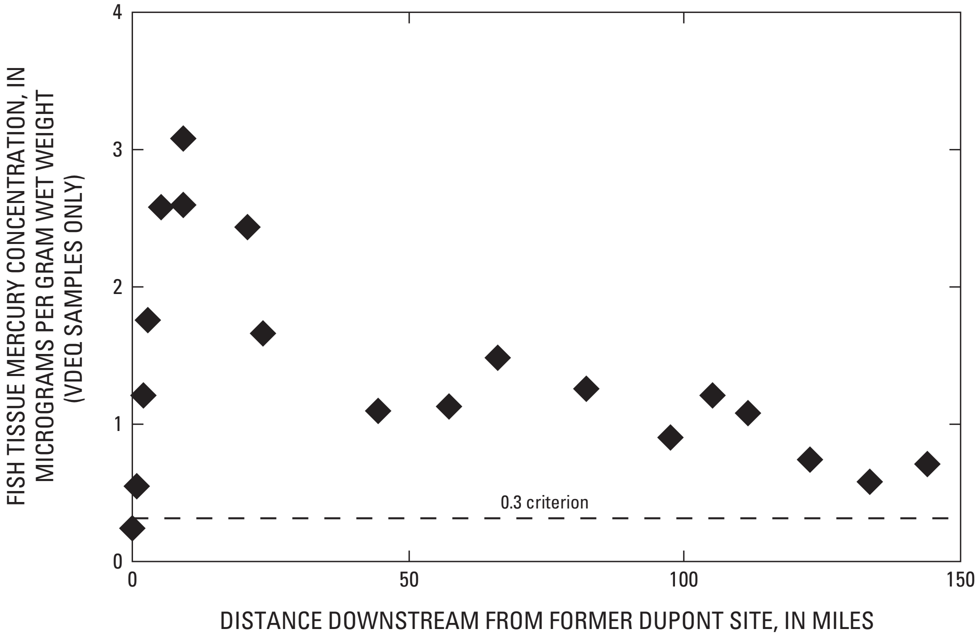



**Figure 12.** Fish tissue mercury concentrations in smallmouth bass 1999-2007, South River, South Fork Shenandoah River, and Shenandoah River, Virginia.

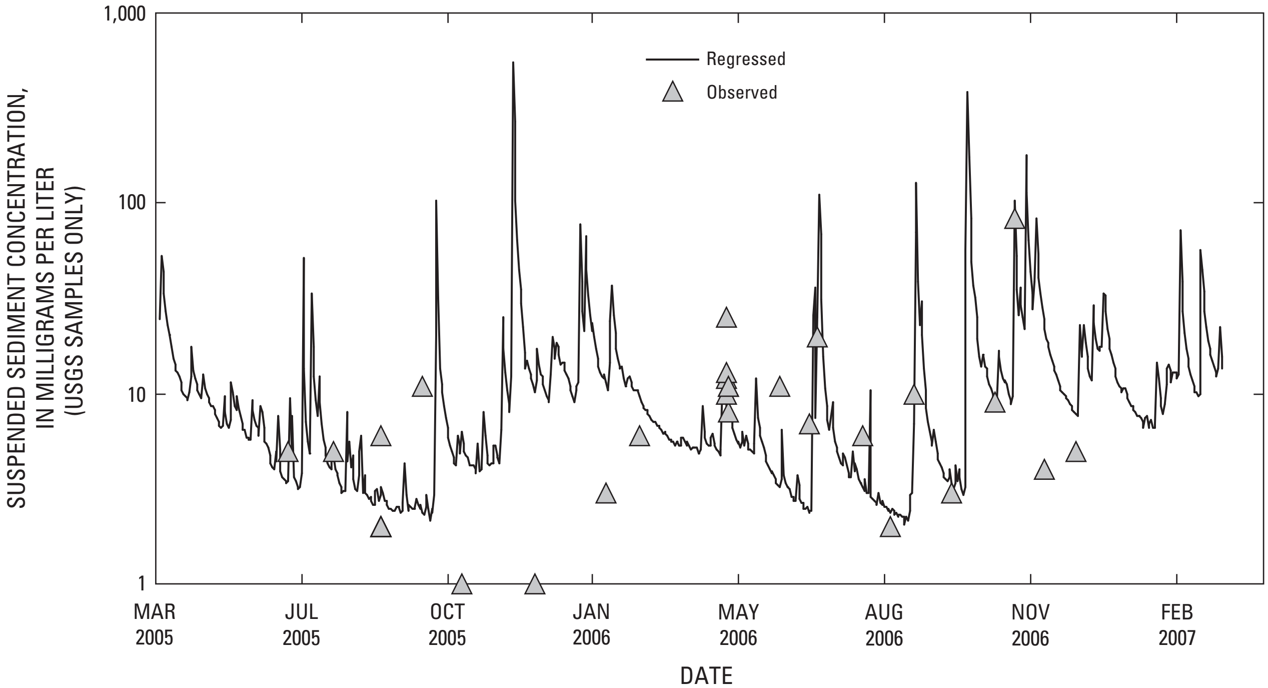



**Figure 13.** Time series of regressed and sampled suspended sediment concentrations, South River at Harriston (USGS station number 01627500), Virginia, April 1, 2005, through March 31, 2007.

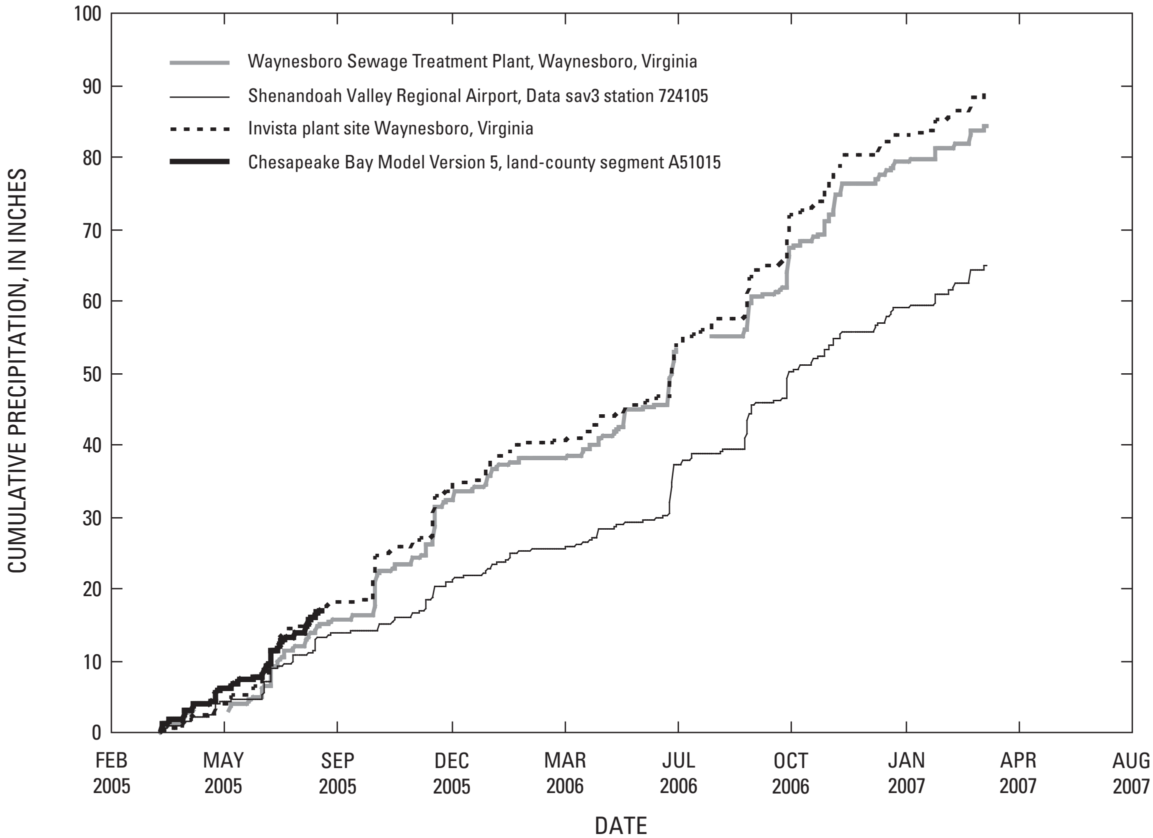



**Figure 14.** Cumulative precipitation at sites in and near the South River watershed, Virginia for the period April 1, 2005, through March 31, 2007. (Chesapeake Bay Watershed Model Version 5 data obtained from the U.S. Environmental Protection Agency Chesapeake Bay Office, Annapolis, Maryland, 2006).

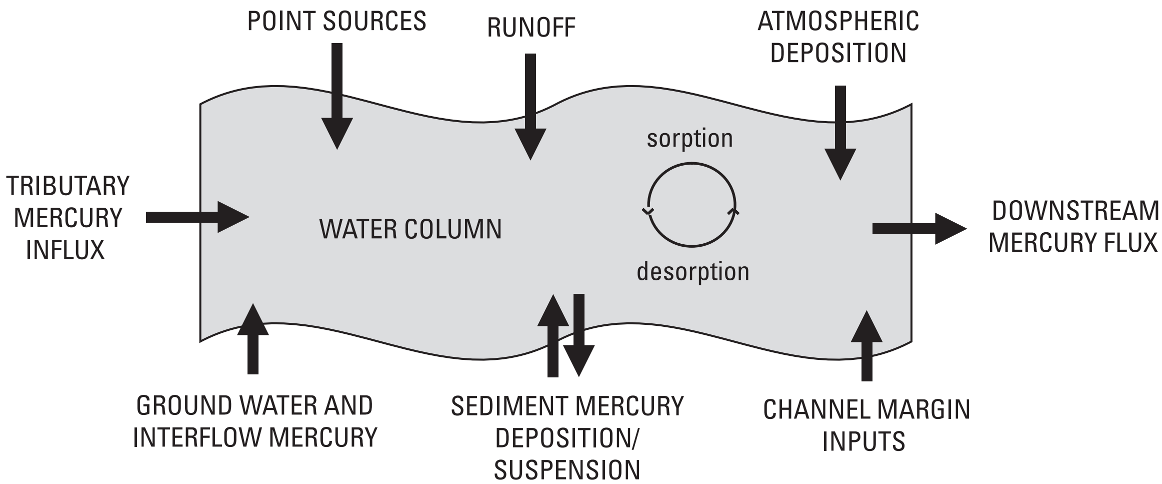
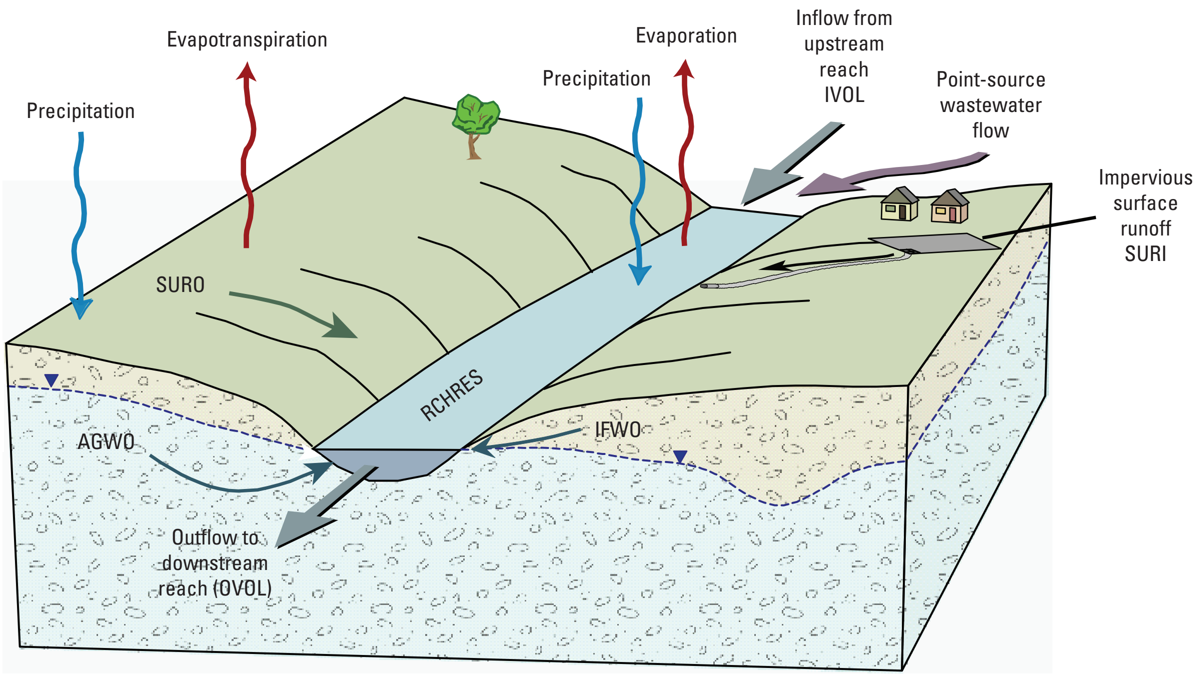



**Figure 15.** Conceptual model of total mercury sources, sinks, and transport in the South River, Virginia.




SURI–Surface runoff from impervious areas
SURO–Surface runoff from pervious areas
IFWO–Interflow
AGWO–Active ground-water flow (base flow)
RCHRES–Stream reach or reservoir segment
IVOL–Inflow volume
OVOL–Outflow volume

**Figure 16.** Schematic showing hydrologic routing in the South River numerical watershed model. [modified from Zarriello and Bent, 2004, figure 9].


**Figure 17.** Location of South River watershed model sub-basins.

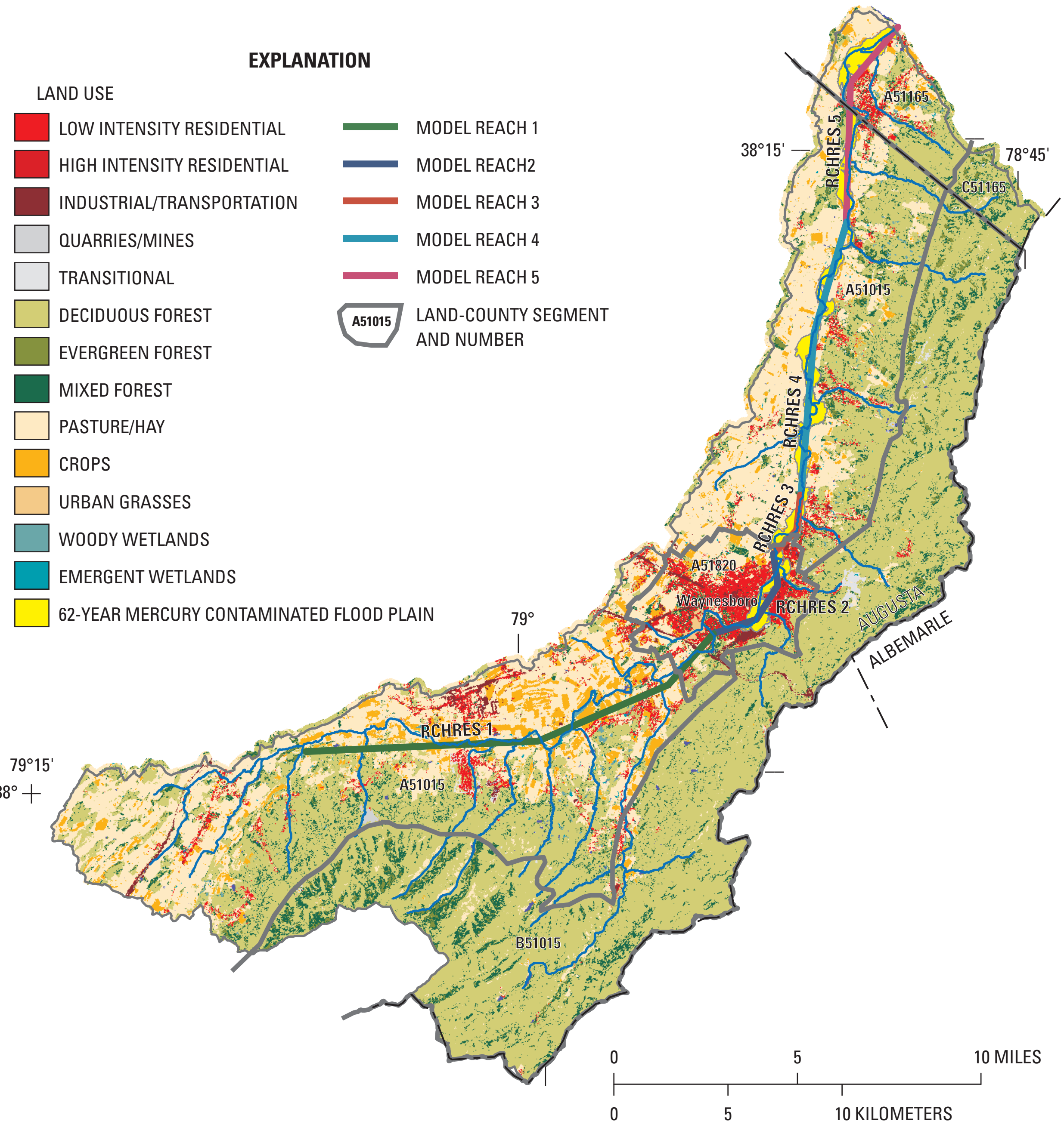



**Figure 18.** Land use in the South River watershed [National Land Cover Dataset, April 27,1999; DuPont Corporate Remediation Group, 2007, South River 62-yr floodplain data layer].

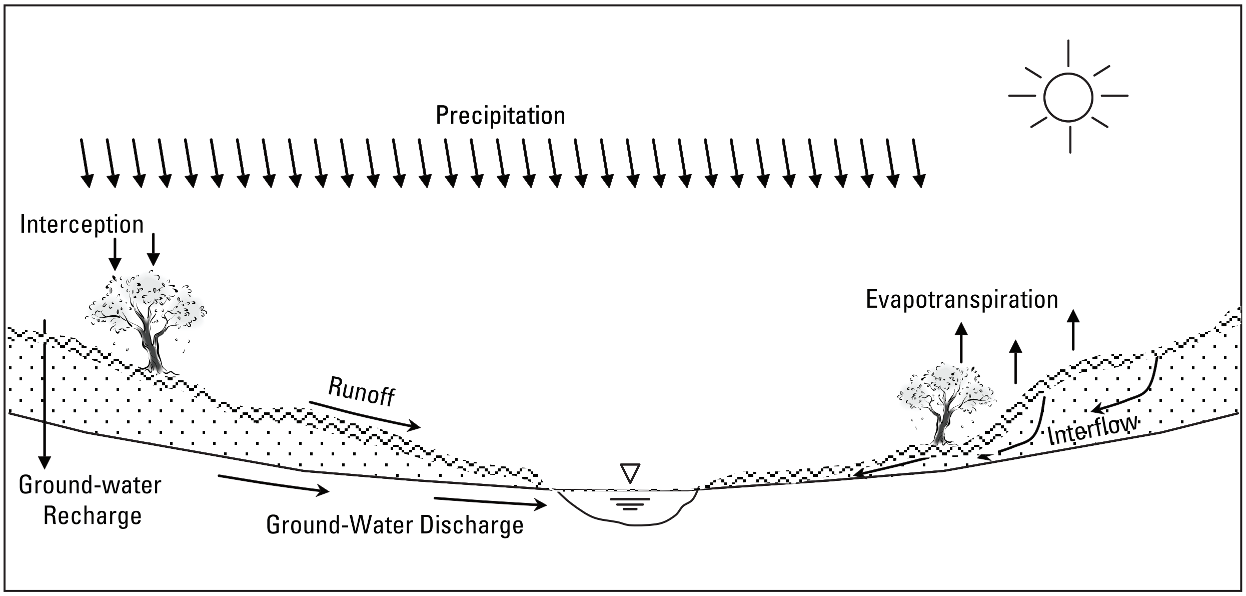



**Figure 19.** Major hydrologic components for pervious land areas and river reaches simulated in the South River numerical watershed model.

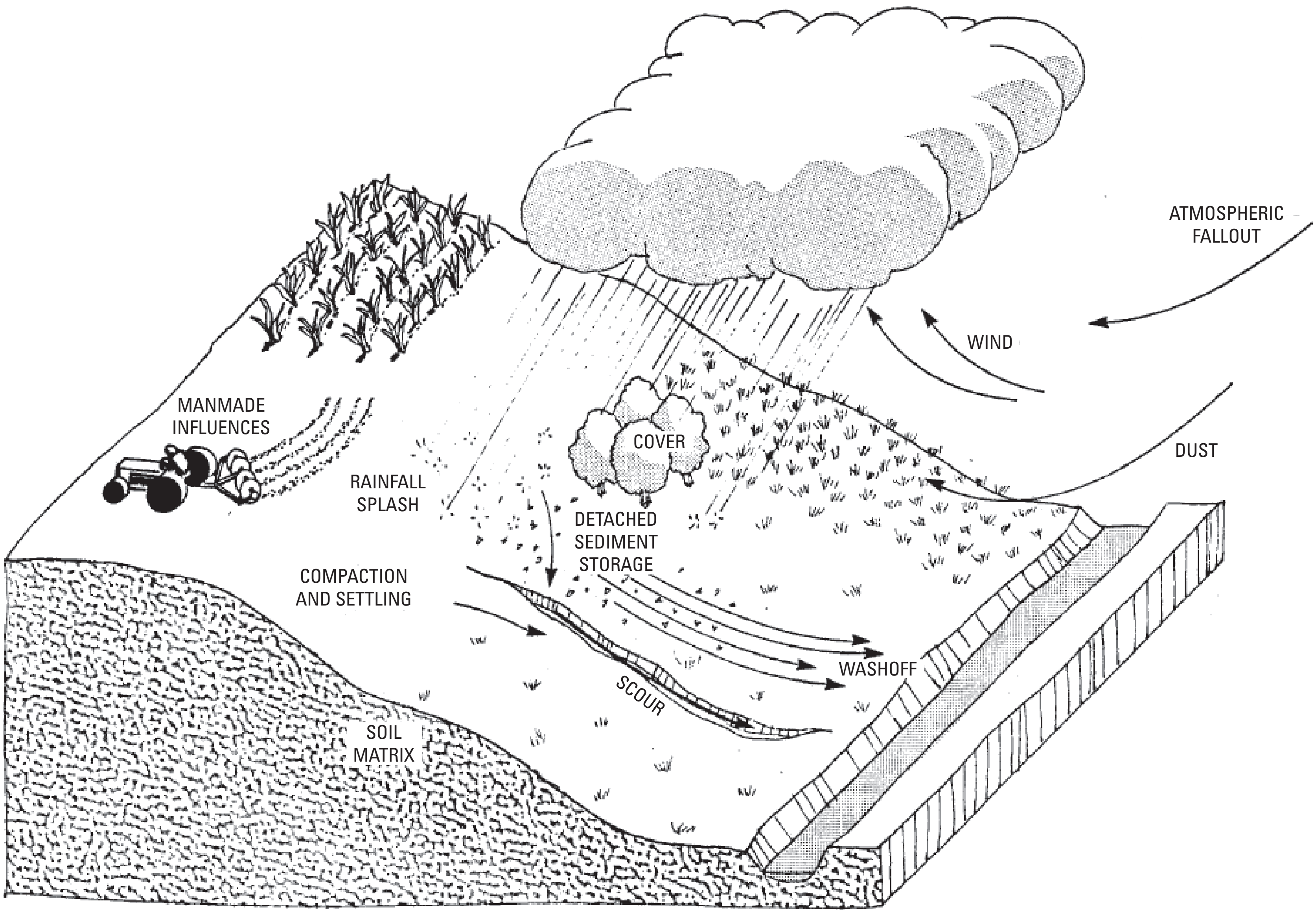



**Figure 20.** Sediment transport processes for pervious land areas. (from Bicknell and others, 2001)

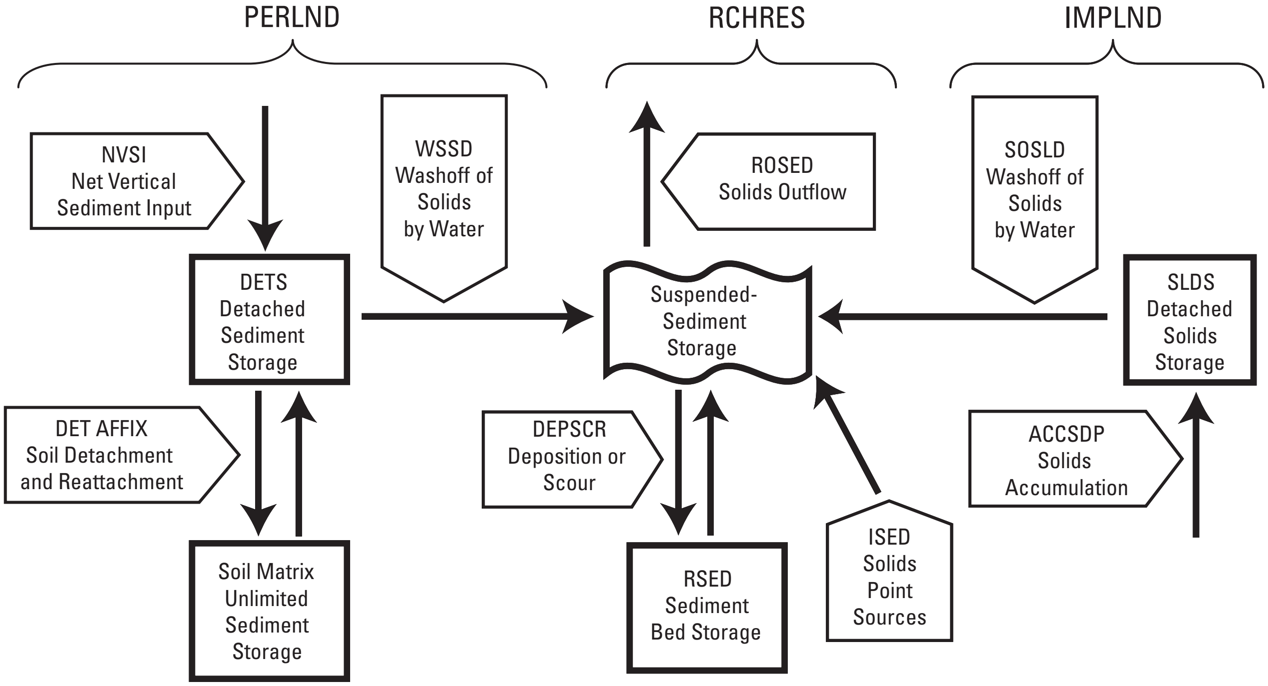



**Figure 21.** Sediment routing processes in the South River numerical watershed model.

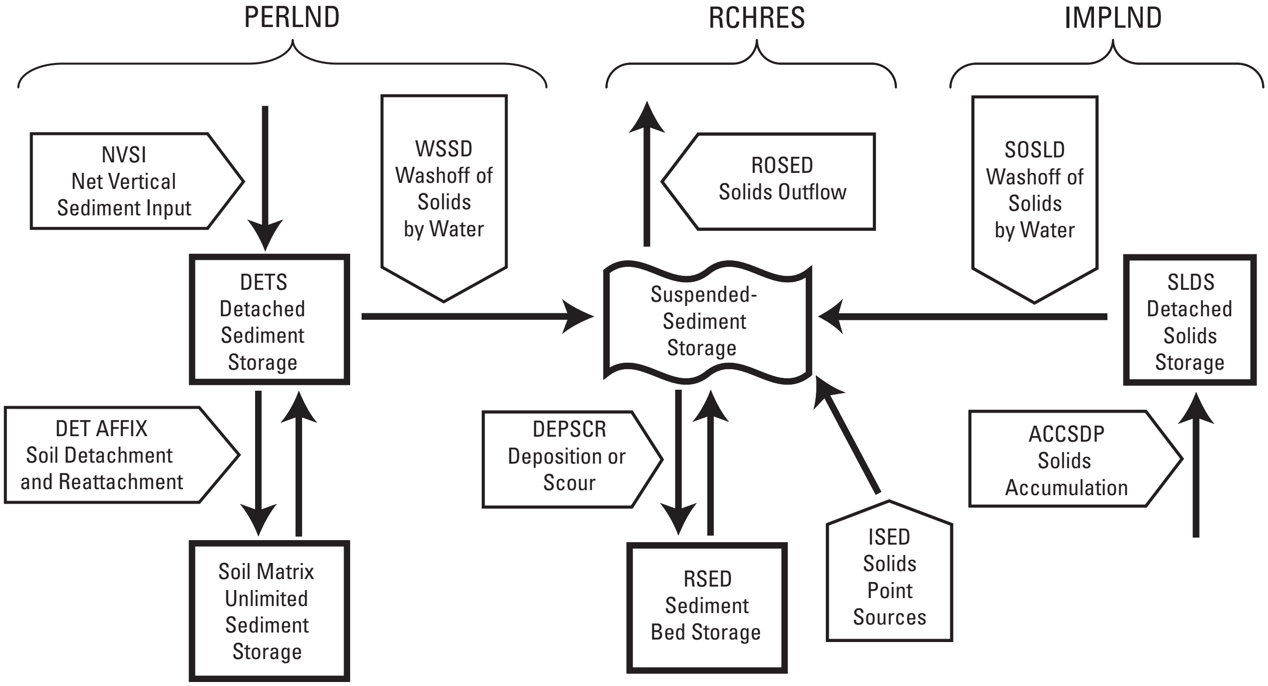



**Figure 21.** Sediment routing processes in the South River numerical watershed model.

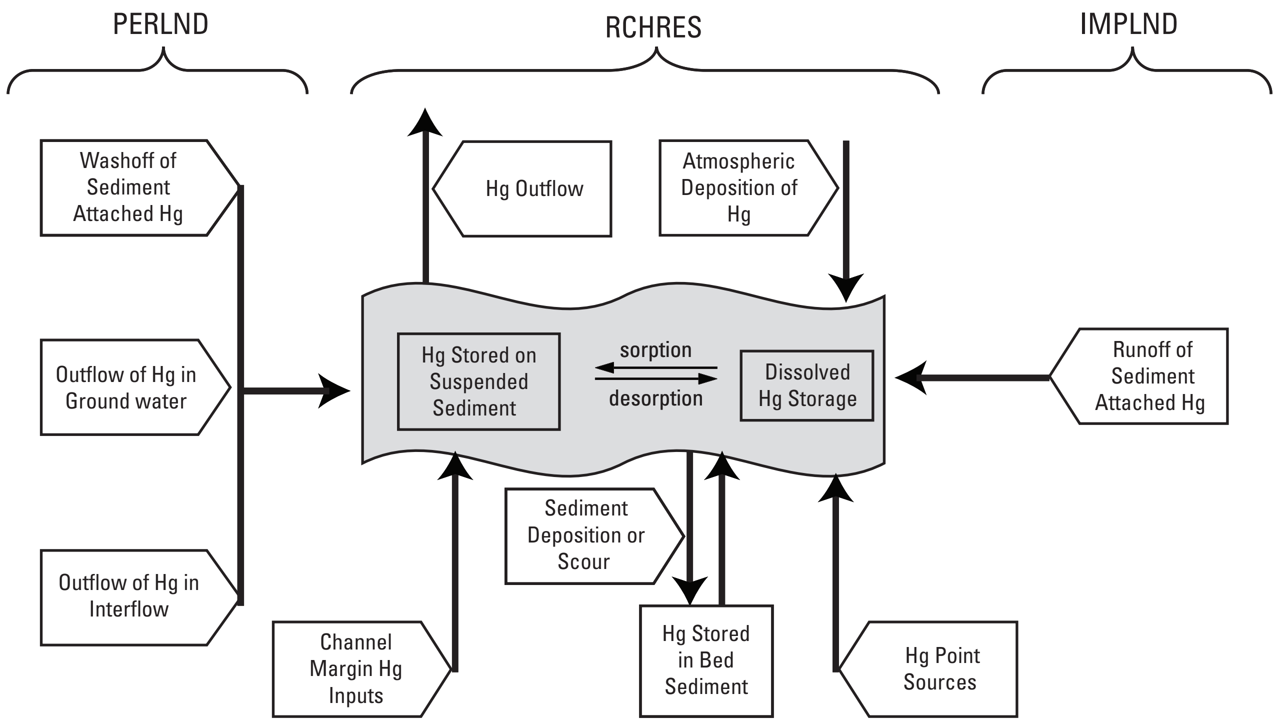



**Figure 22.** Mercury routing in the South River numerical watershed model.

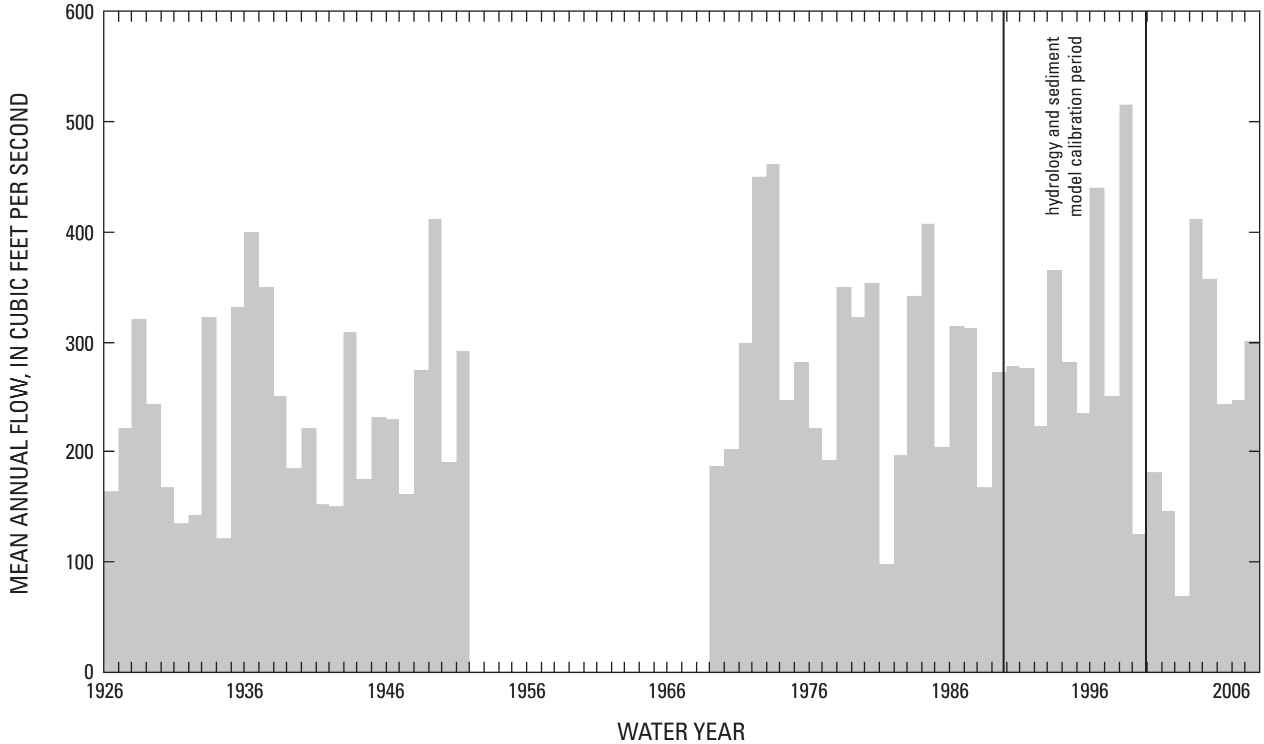



**Figure 23.** Observed mean annual flow, South River at Harriston (USGS station number 01627500), Virginia, water years 1926-2007.

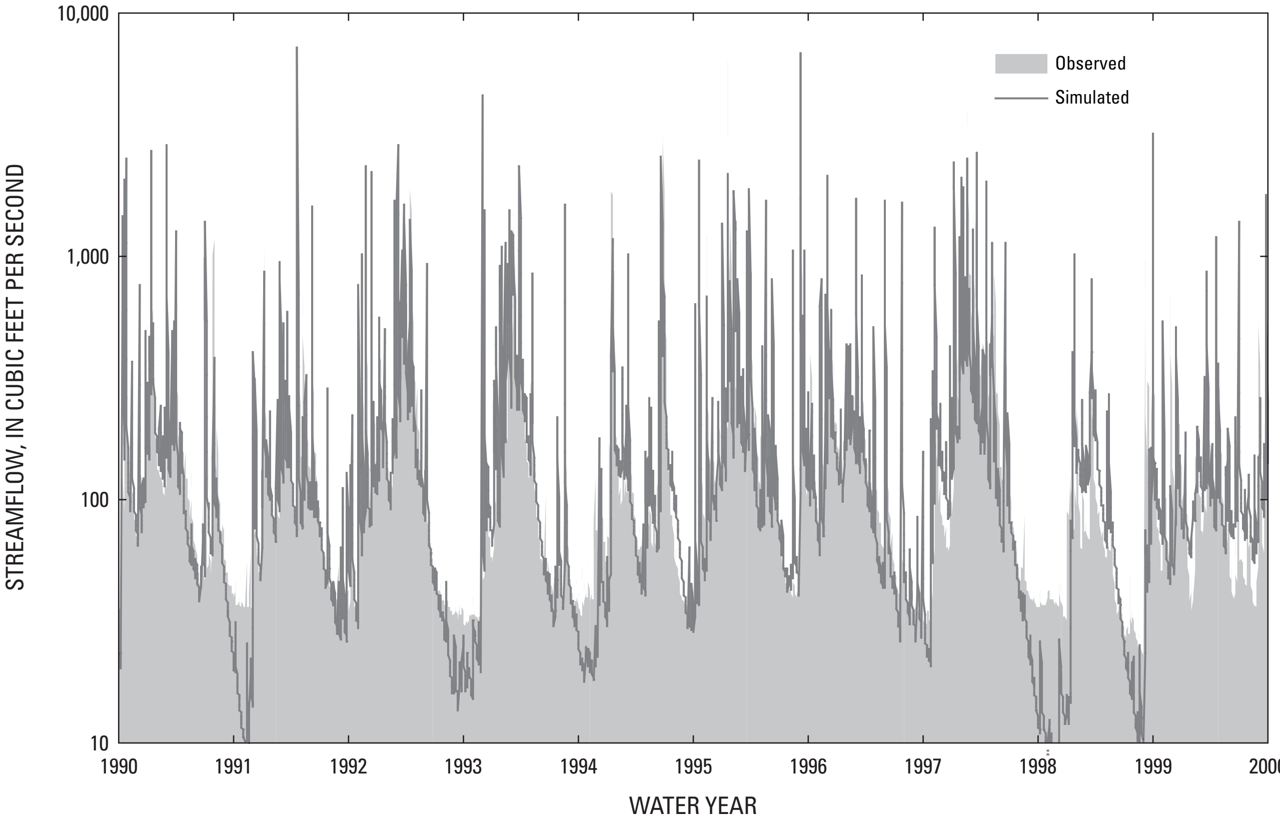



**Figure 24.** Simulated and observed daily streamflow for the calibration period water years 1991-2000, calibrated model, South River near Waynesboro (USGS station number 01626000), Virginia.

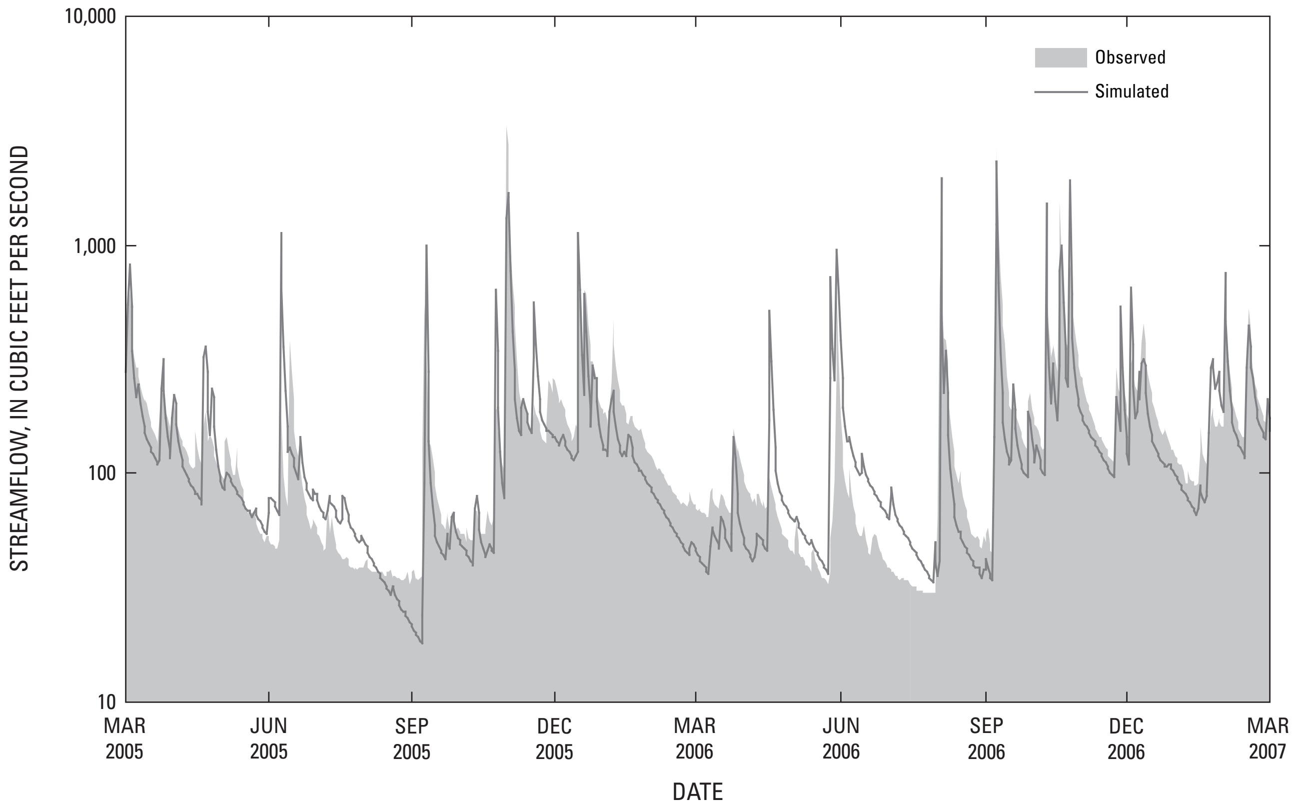



**Figure 25.** Simulated and observed daily streamflow during the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro (USGS station number. 01626000), Virginia.

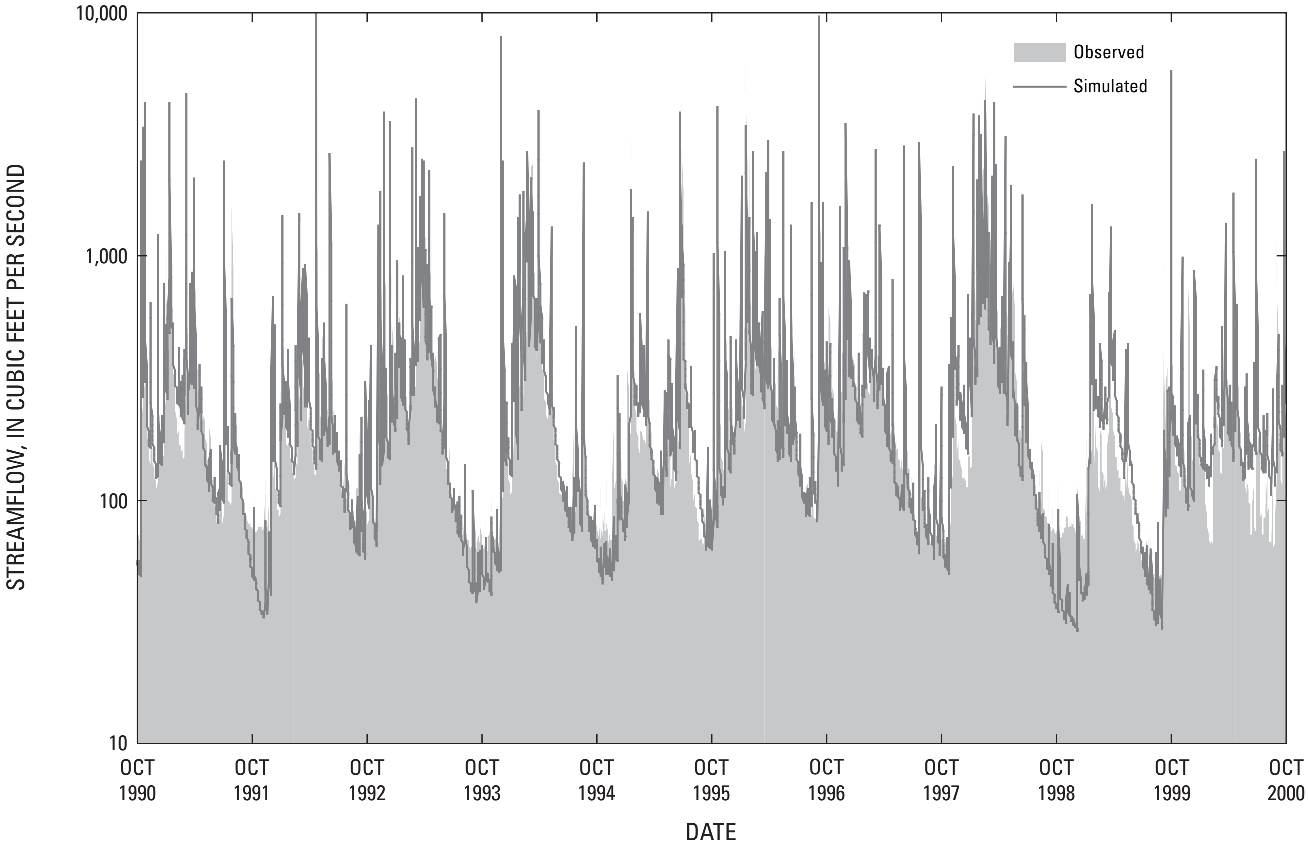



**Figure 26.** Simulated and observed daily streamflow during the calibration period water years 1991-2000, calibrated model, South River at Harriston (USGS station number 01627500), Virginia.

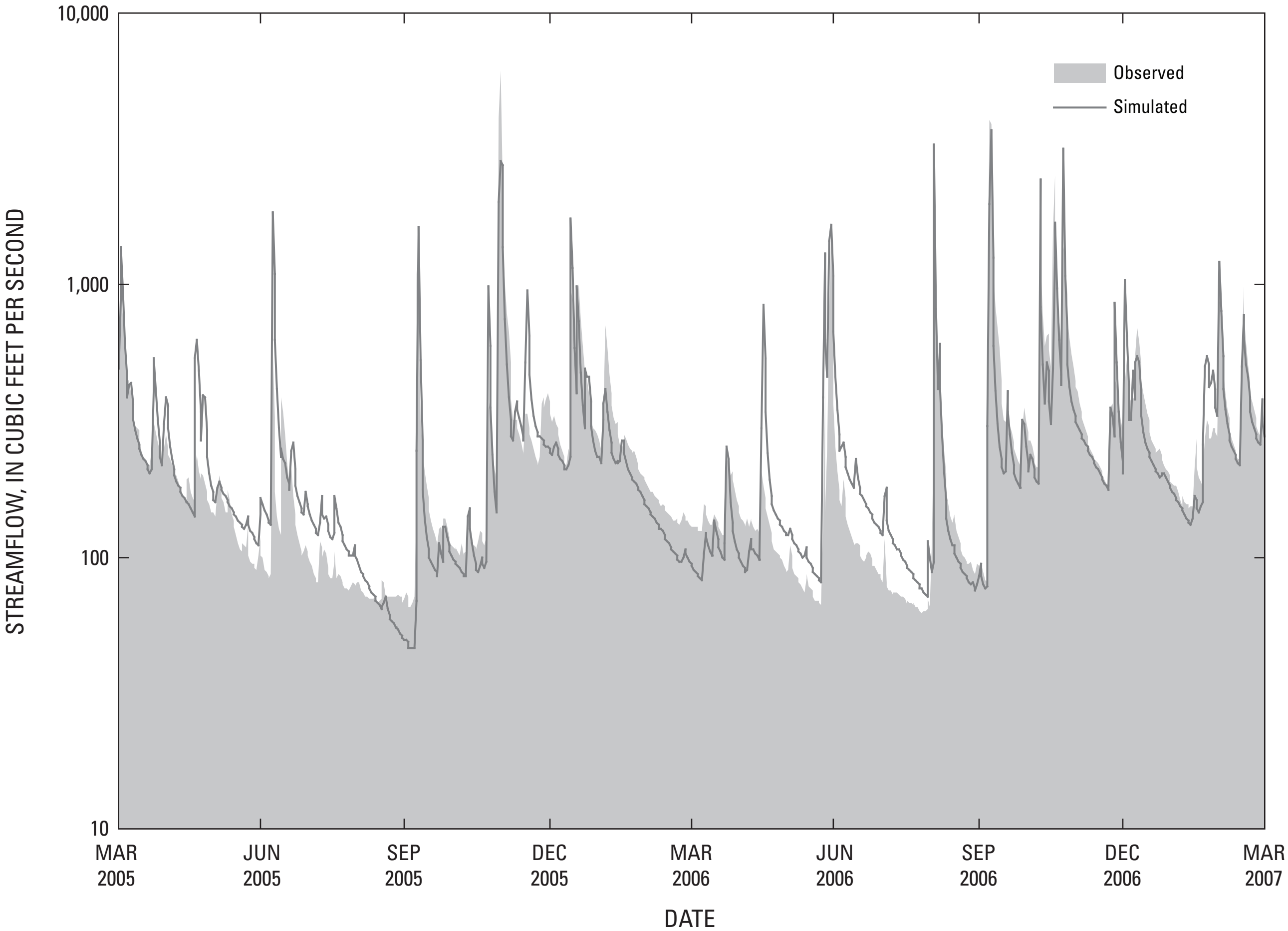



**Figure 27.** Simulated and observed daily streamflow for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston (USGS station number 01627500), Virginia.

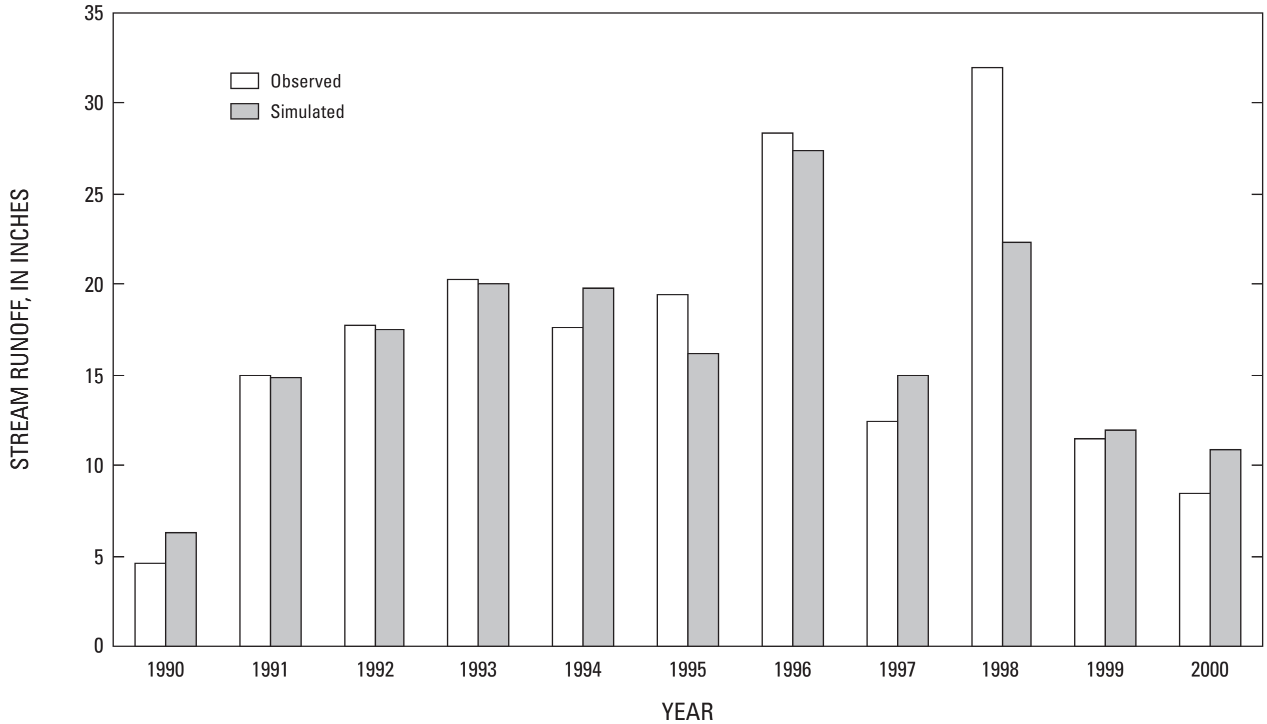



**Figure 28.** Simulated and observed annual runoff during the calibration period water years 1991-2000, calibrated model, South River near Waynesboro (USGS station number 01626000), Virginia.

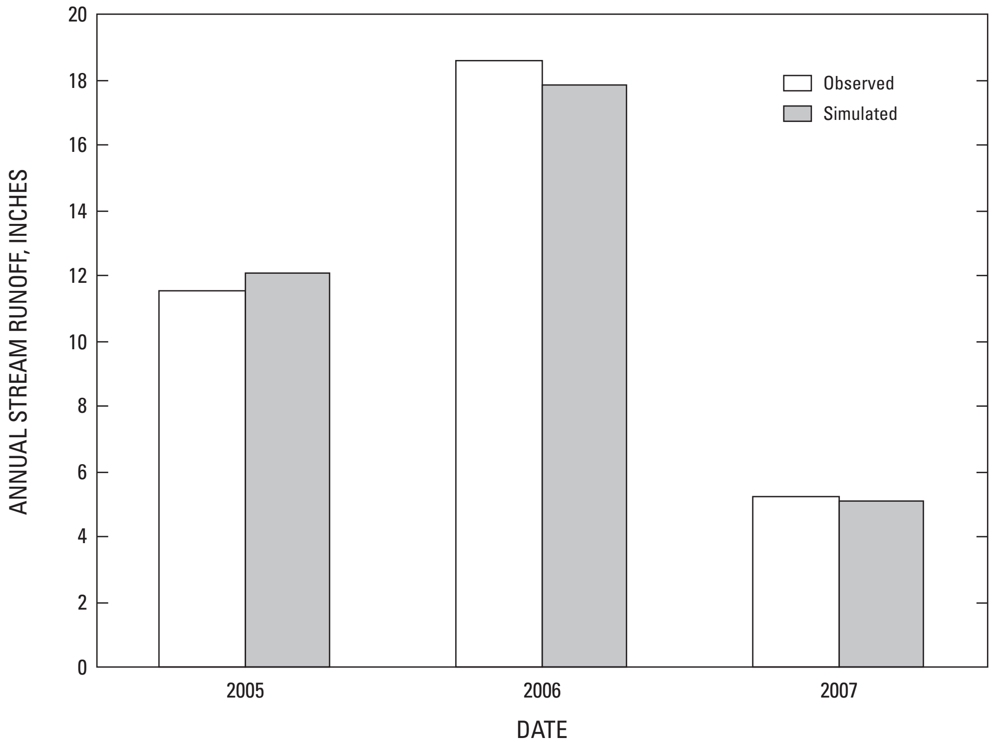



**Figure 29.** Simulated and observed total runoff during the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro (USGS station number 01626000), Virginia.

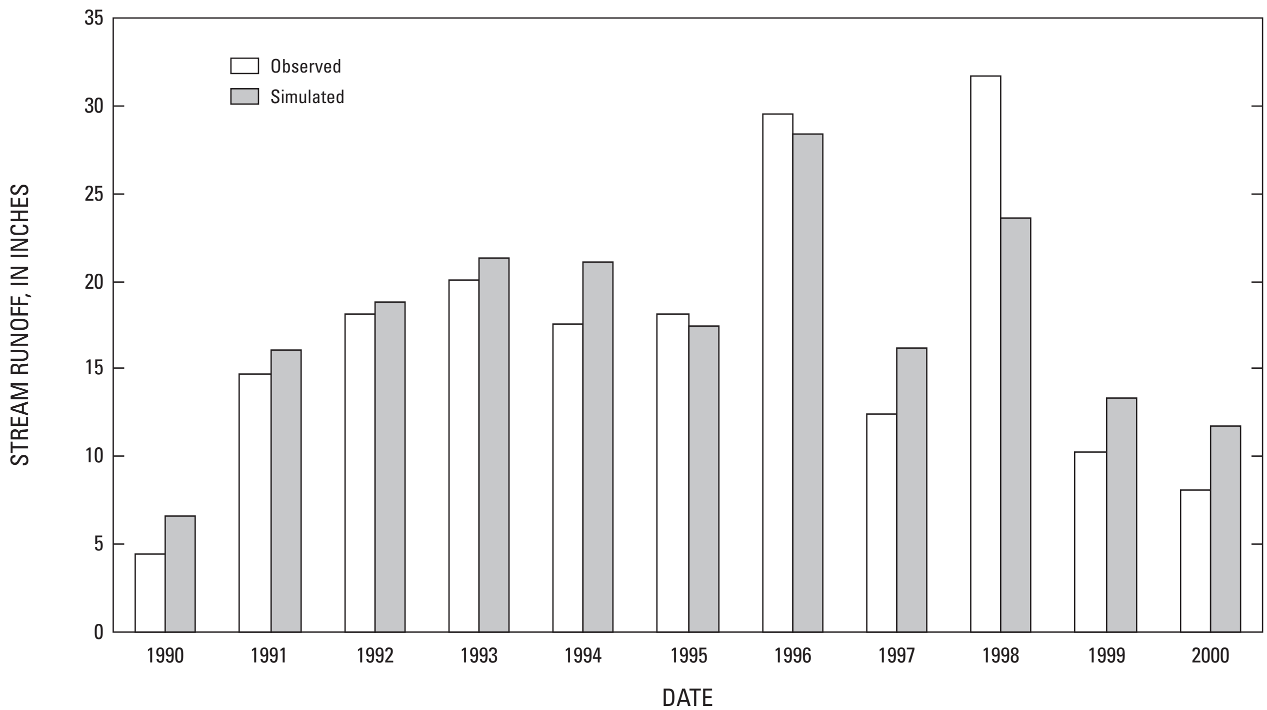



**Figure 30.** Simulated and observed annual runoff during the calibration period water years 1991-2000, calibrated, South River at Harriston (USGS station number 01627500), Virginia.

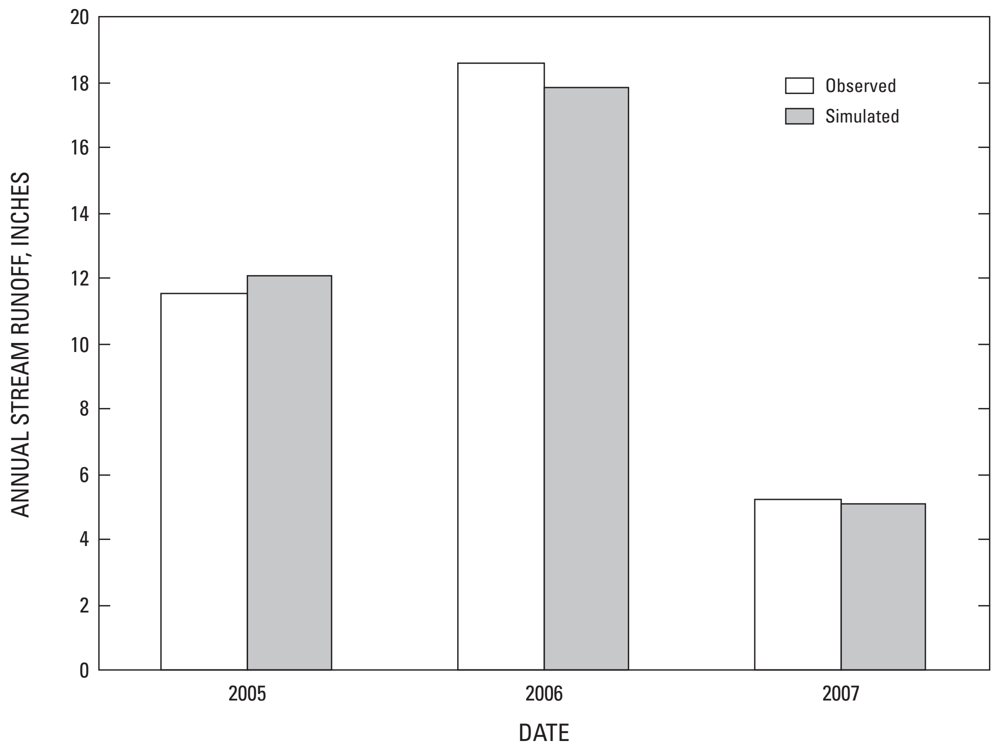



**Figure 31.** Simulated and observed total runoff during the verification period April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston (USGS station number 01627500), Virginia.

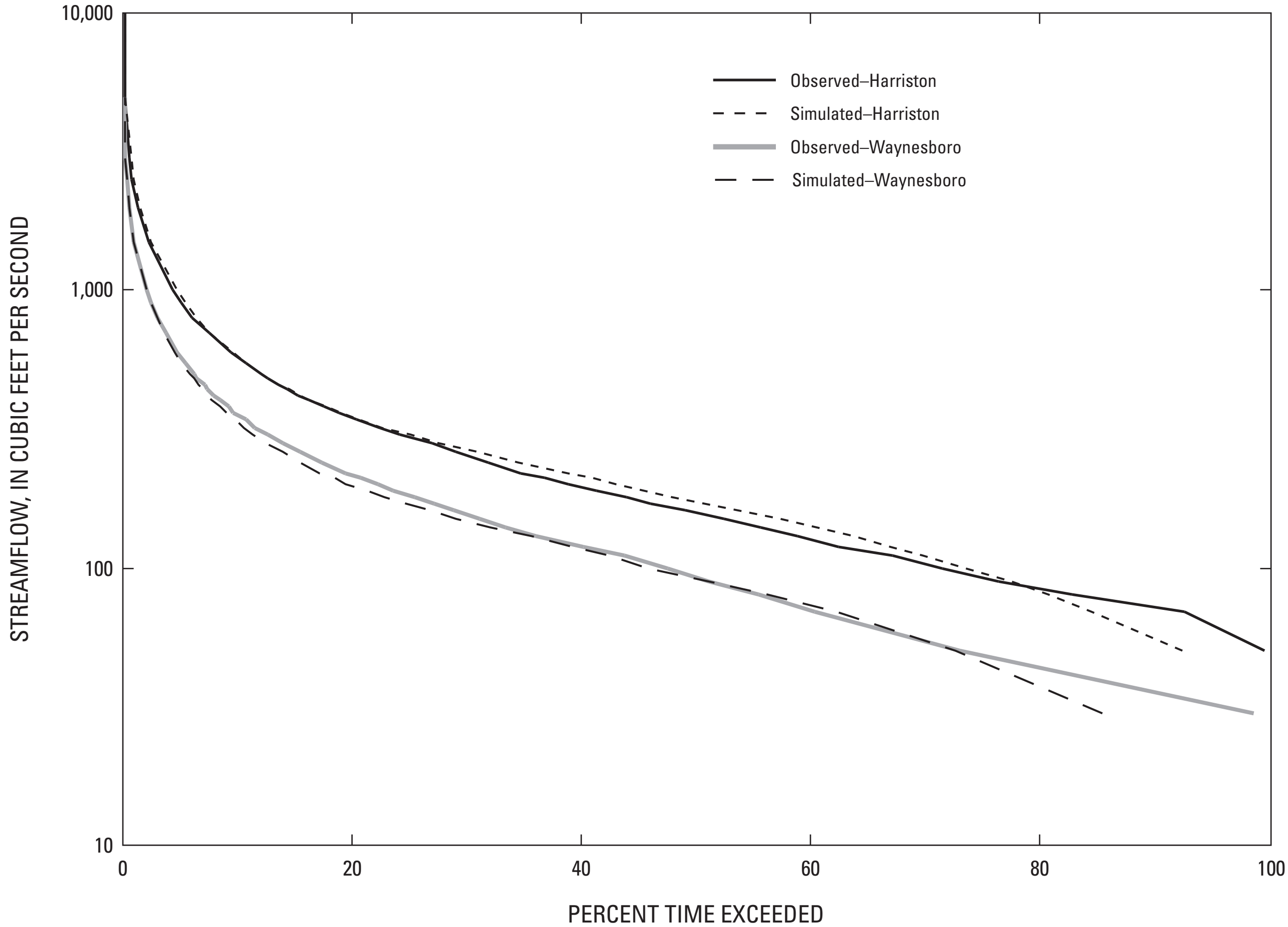



**Figure 32.** Flow duration curves for observed and simulated streamflow, calibration period water years 1991-2000, calibrated model, for the South River near Waynesboro (USGS station number 01626000) and at Harriston (USGS station number 01627500), Virginia.

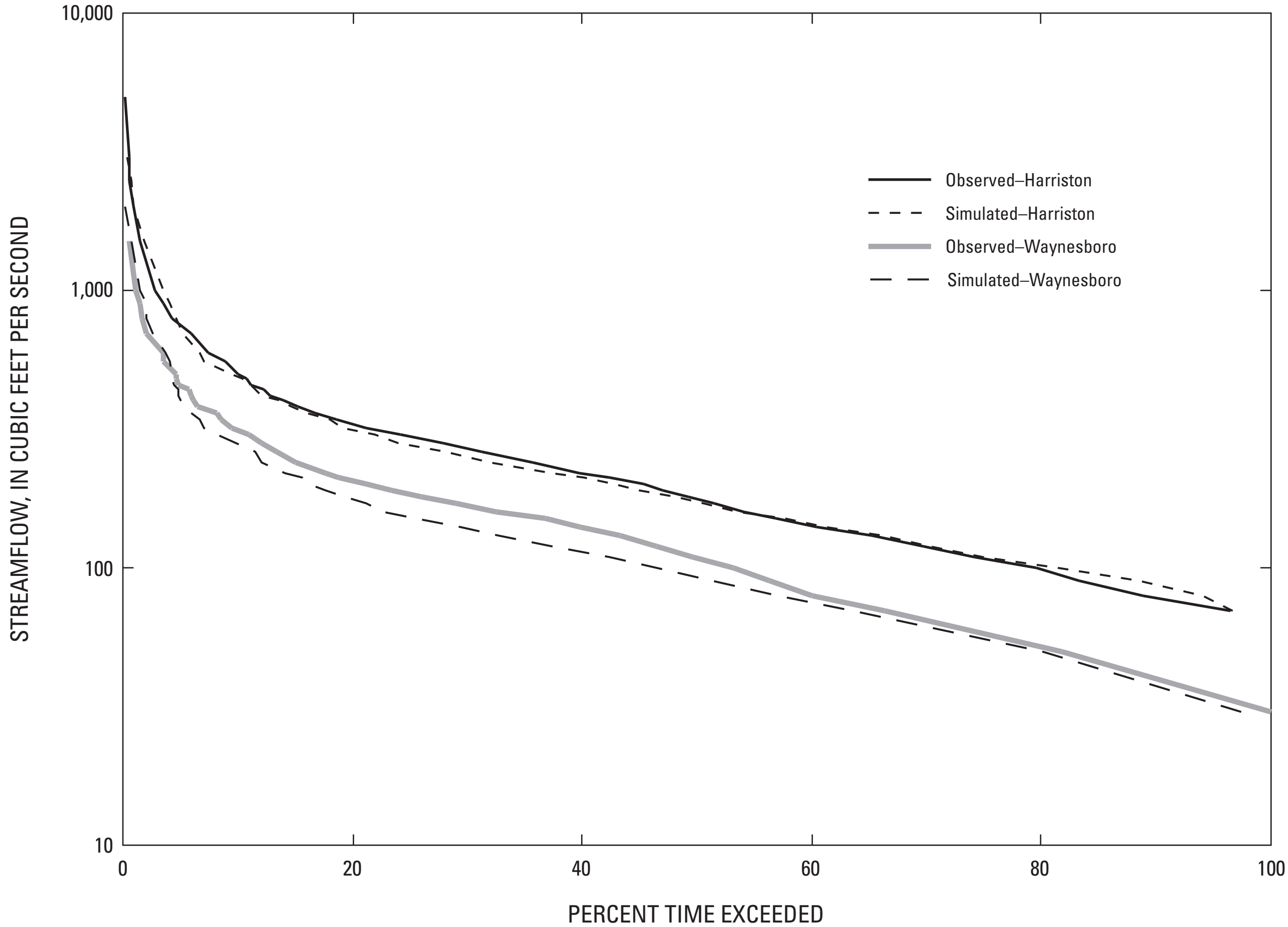



**Figure 33.** Flow duration curves for observed and simulated daily streamflow, calibrated model, South River near Waynesboro (USGS station number 01626000) and at Harriston (USGS station number 01627500), Virginia, verification period April 1, 2005, through March 31, 2007.

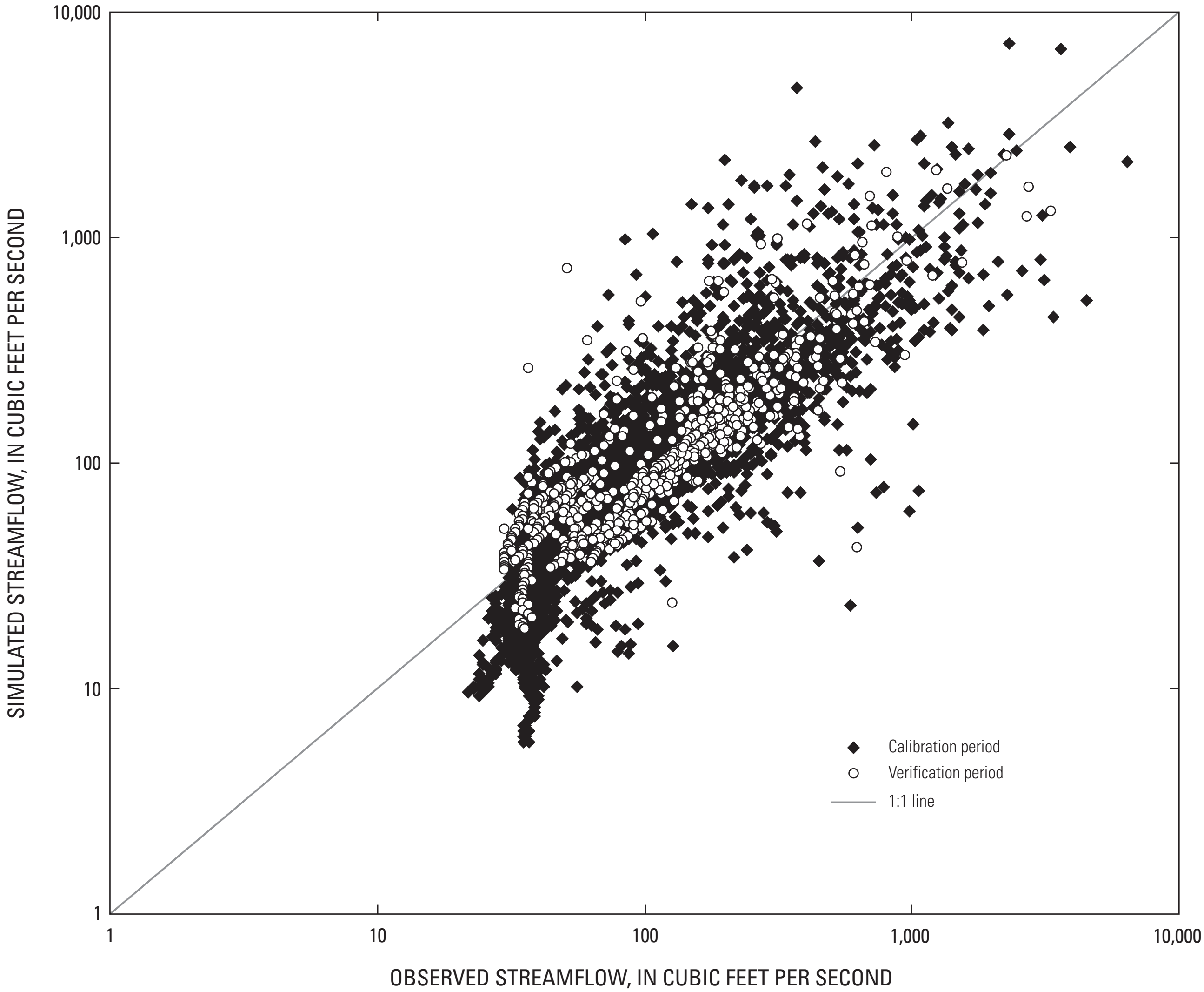



**Figure 34.** 1:1 comparison of simulated and observed daily streamflow, calibrated model, South River near Waynesboro (USGS station number 01626000), Virginia, water years 1991-2000 and April 2005 through March 2007.

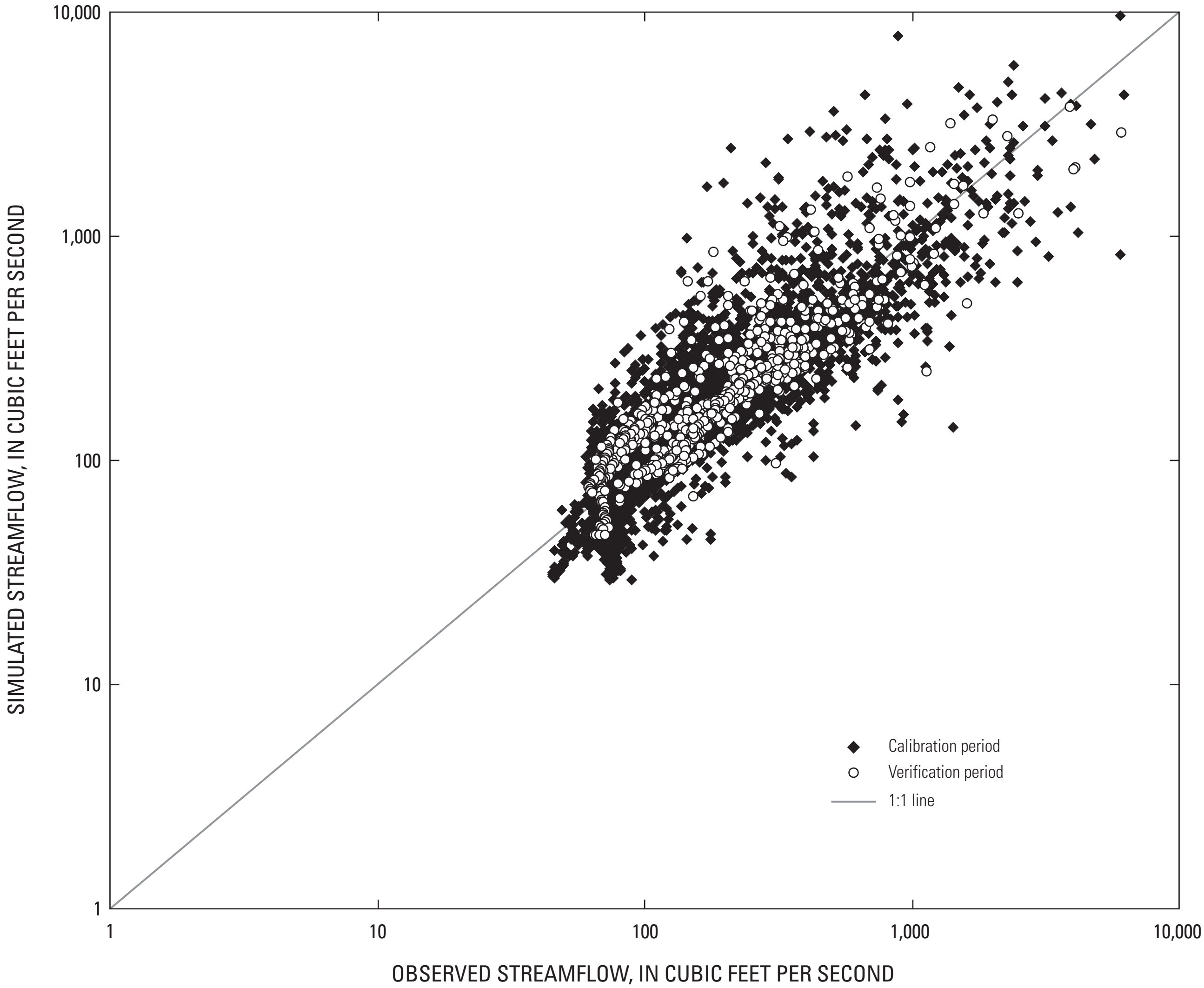



**Figure 35.** 1:1 comparison of simulated and observed daily streamflow, calibrated model, South River at Harriston (USGS station number 01627500), Virginia, water years 1991-2000 and April 2005 through March 2007.

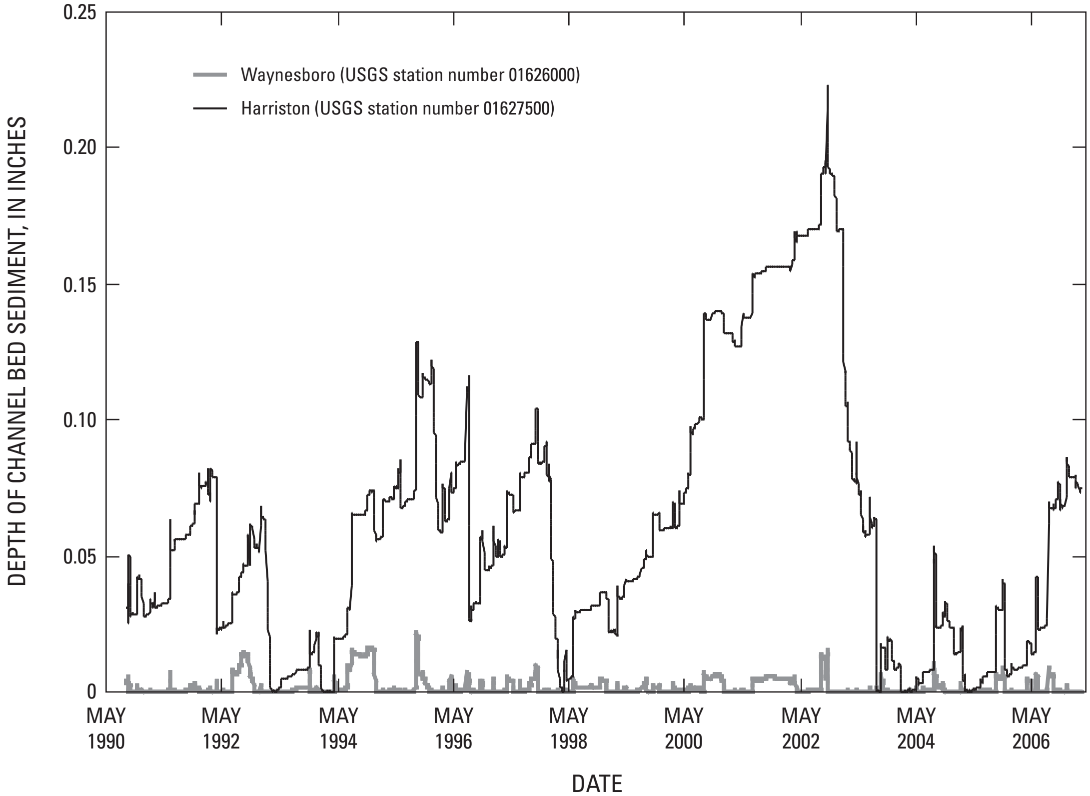



**Figure 36.** Simulated depth of sediment in model river reaches 1 and 4, calibrated South River model, water years 1991-2000.

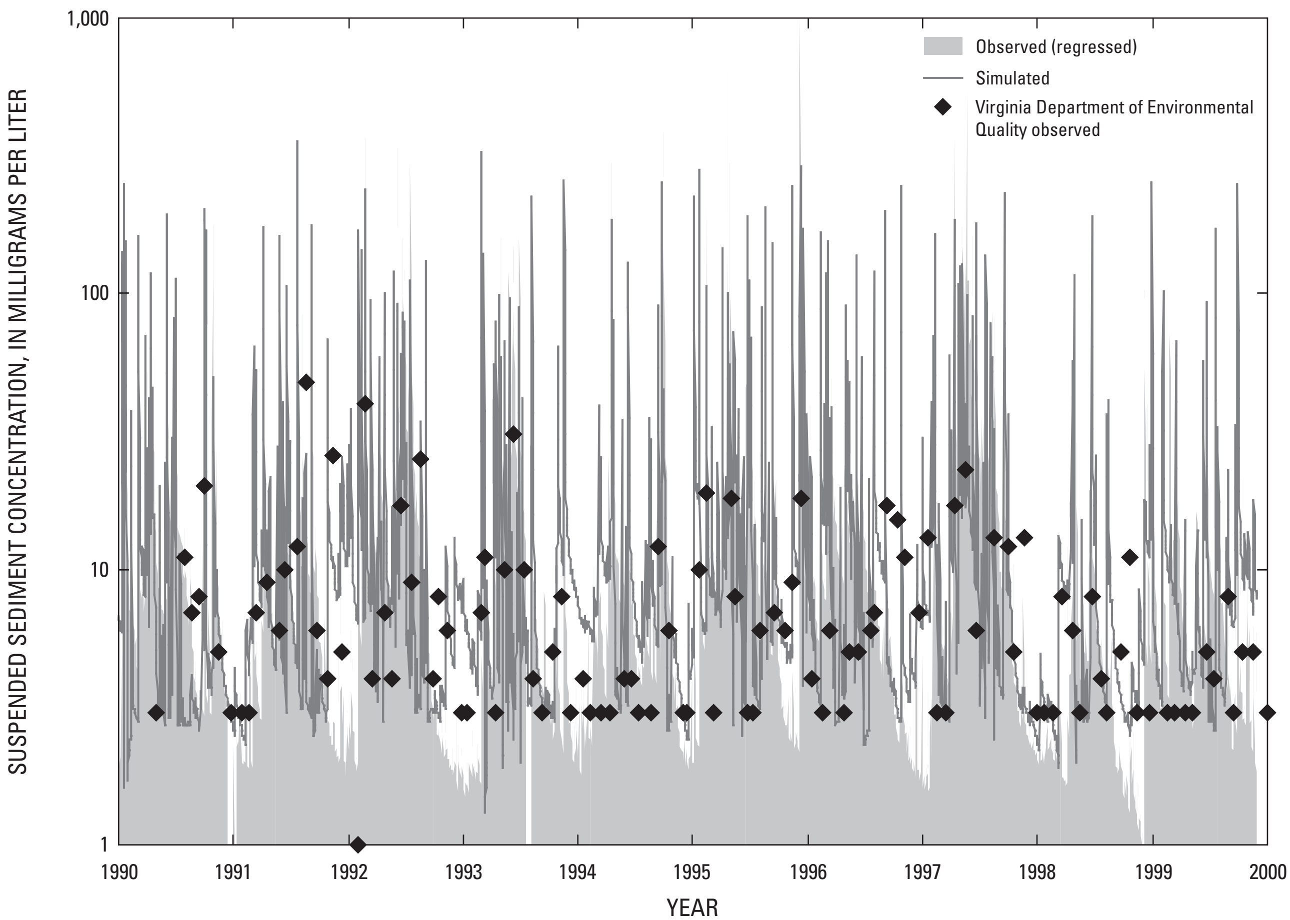



**Figure 37.** Simulated daily, observed (regressed), and sampled suspended sediment concentrations for the calibration period, water years 1991-2000, South River near Waynesboro (USGS station number 01626000), Virginia.

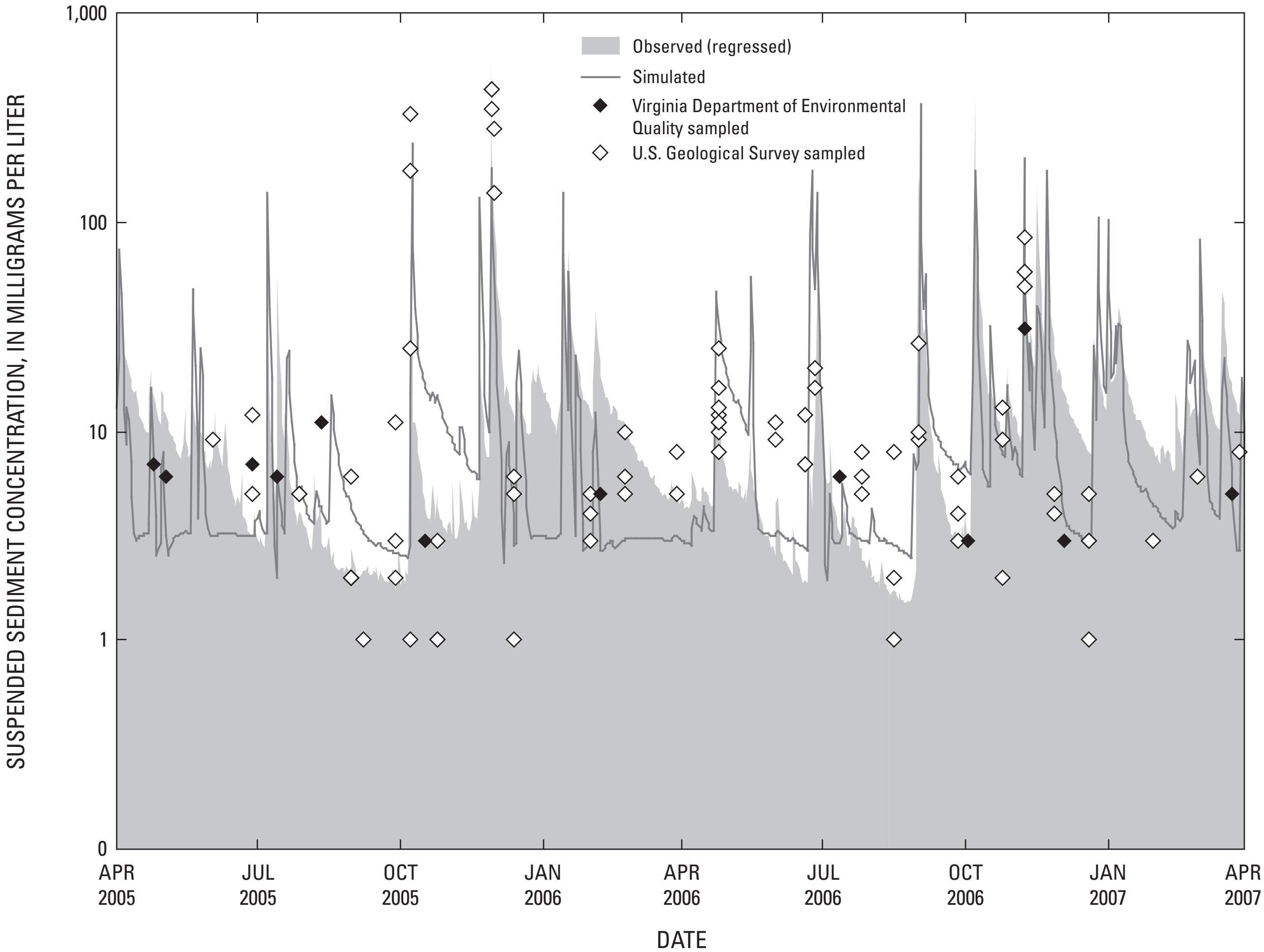



**Figure 38.** Simulated daily, observed (regressed), and sampled suspended sediment concentrations for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro (USGS station number 01626000), Virginia.

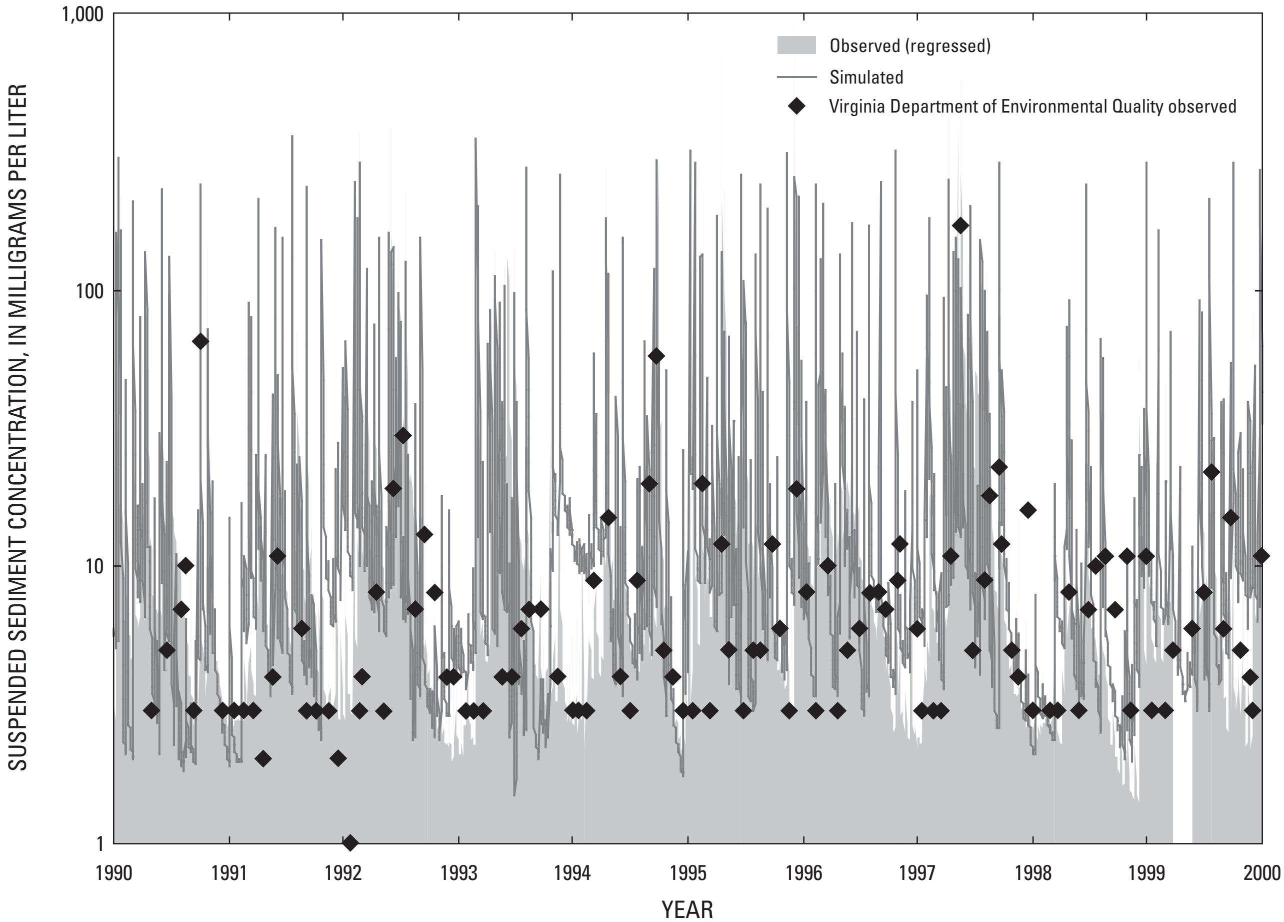



**Figure 39.** Simulated and observed (regressed) suspended sediment concentrations for the calibration period water years 1991-2000, calibrated model, South River at Harriston (USGS station number 01627500), Virginia.

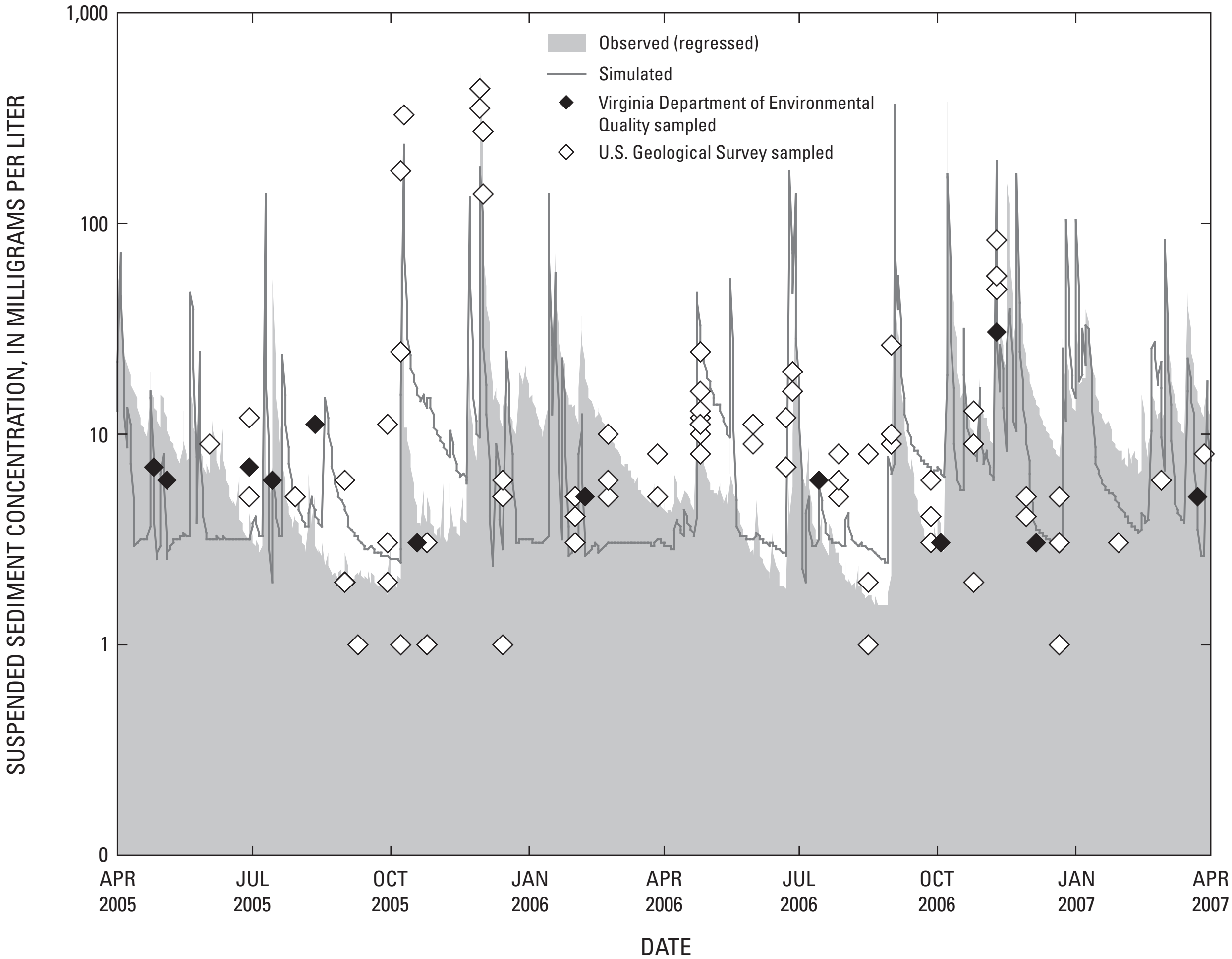



**Figure 40.** Simulated and observed (regressed) suspended sediment concentrations for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston (USGS station number 01627500), Virginia.

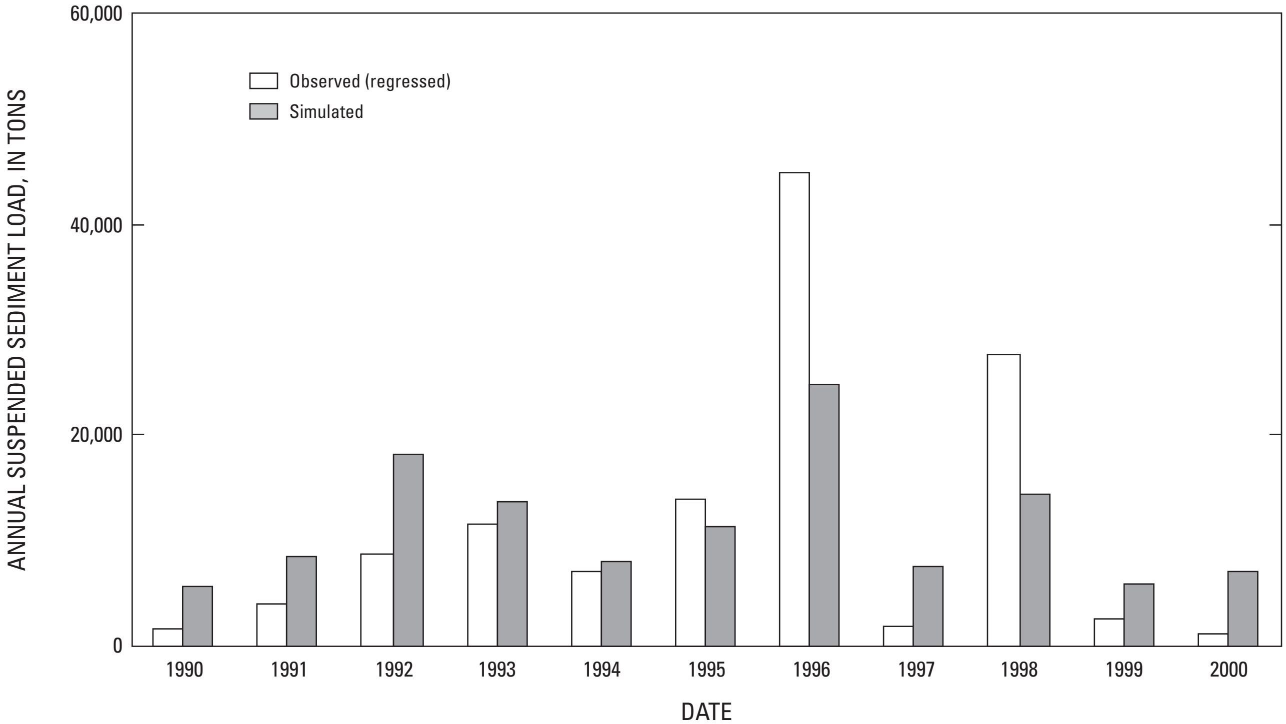



**Figure 41.** Annual simulated and observed (regressed) suspended sediment loads for the calibration period water years 1991-2000, calibrated model, South River near Waynesboro (USGS station number 01626000), Virginia.

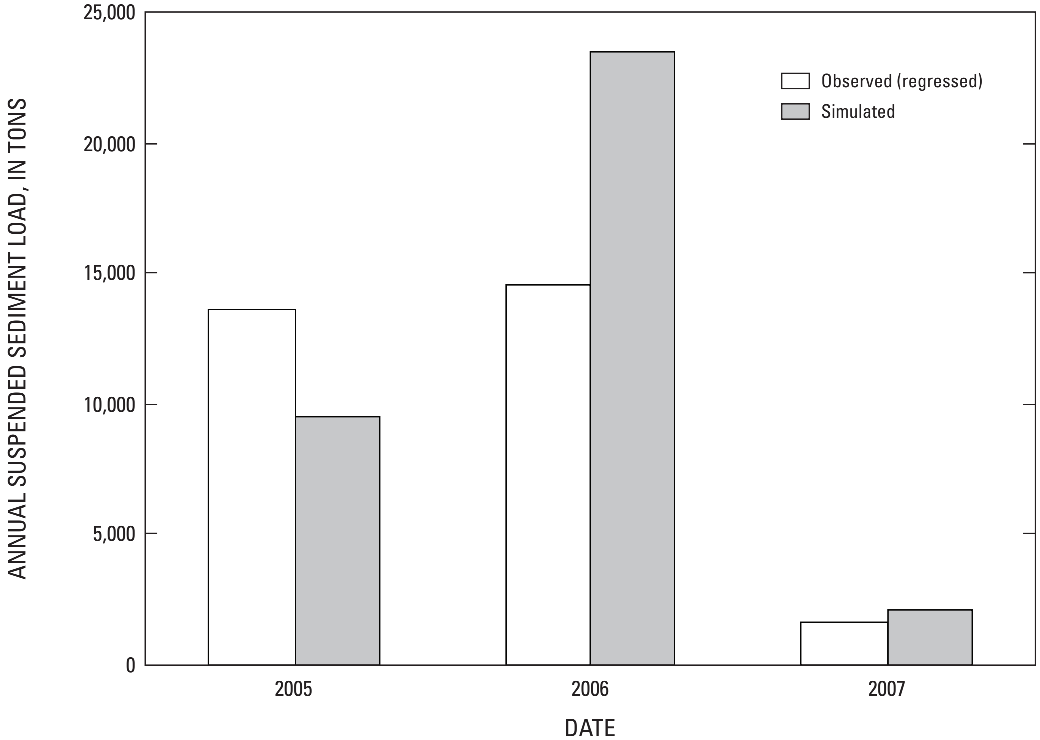



**Figure 42.** Annual simulated and observed (regressed) suspended sediment loads for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro (USGS station number 01626000), Virginia.

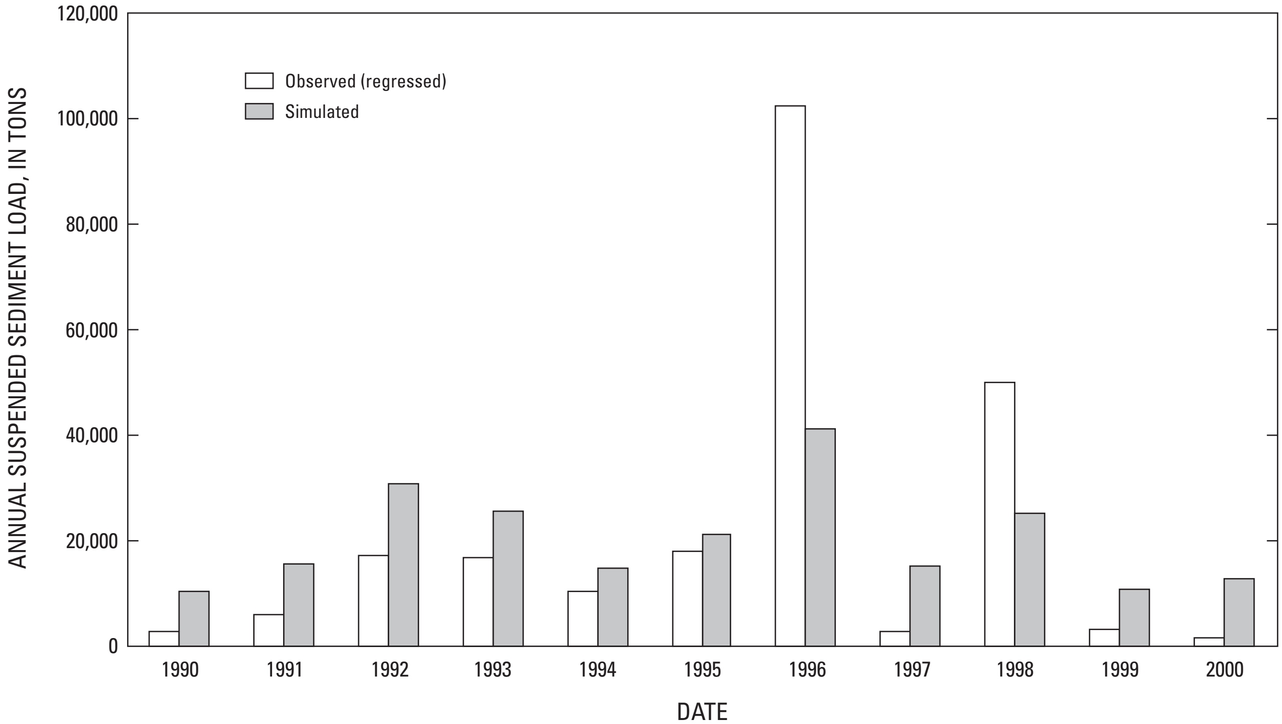



**Figure 43.** Annual simulated and observed (regressed) suspended sediment loads for the calibration period, water years 1991-2000, calibrated model, South River at Harriston (USGS station number 01627500), Virginia.

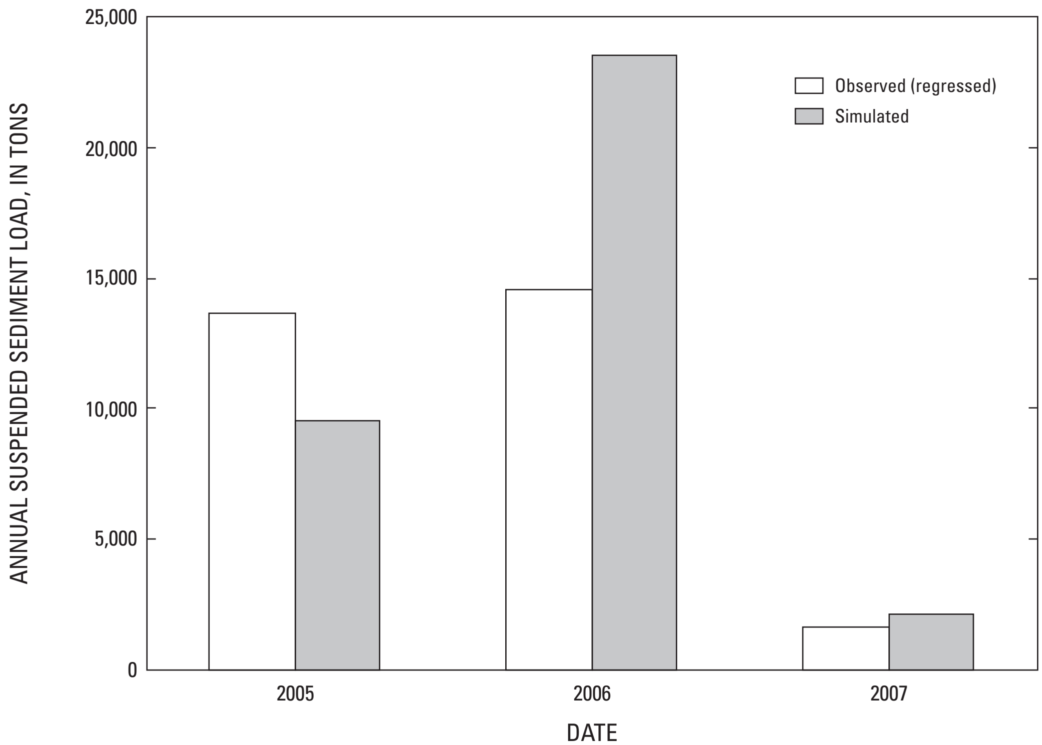



**Figure 44.** Annual simulated and observed (regressed) suspended sediment loads for the verification period, April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston (USGS station number 01627500), Virginia.

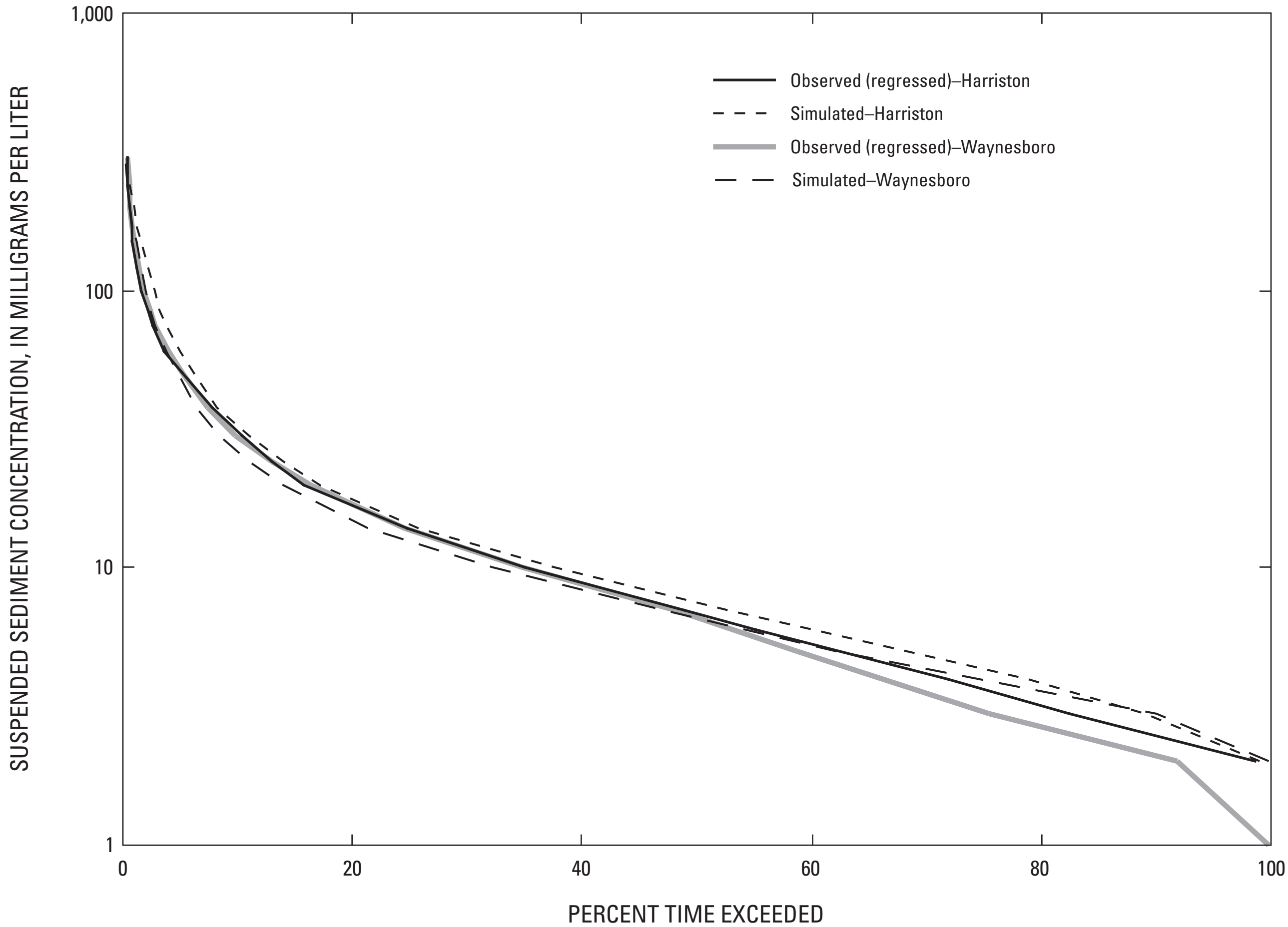



**Figure 45.** Duration plots for simulated and observed (regressed) daily suspended sediment concentrations, calibration period water years 1991-2000, calibrated model, South River, Virginia.

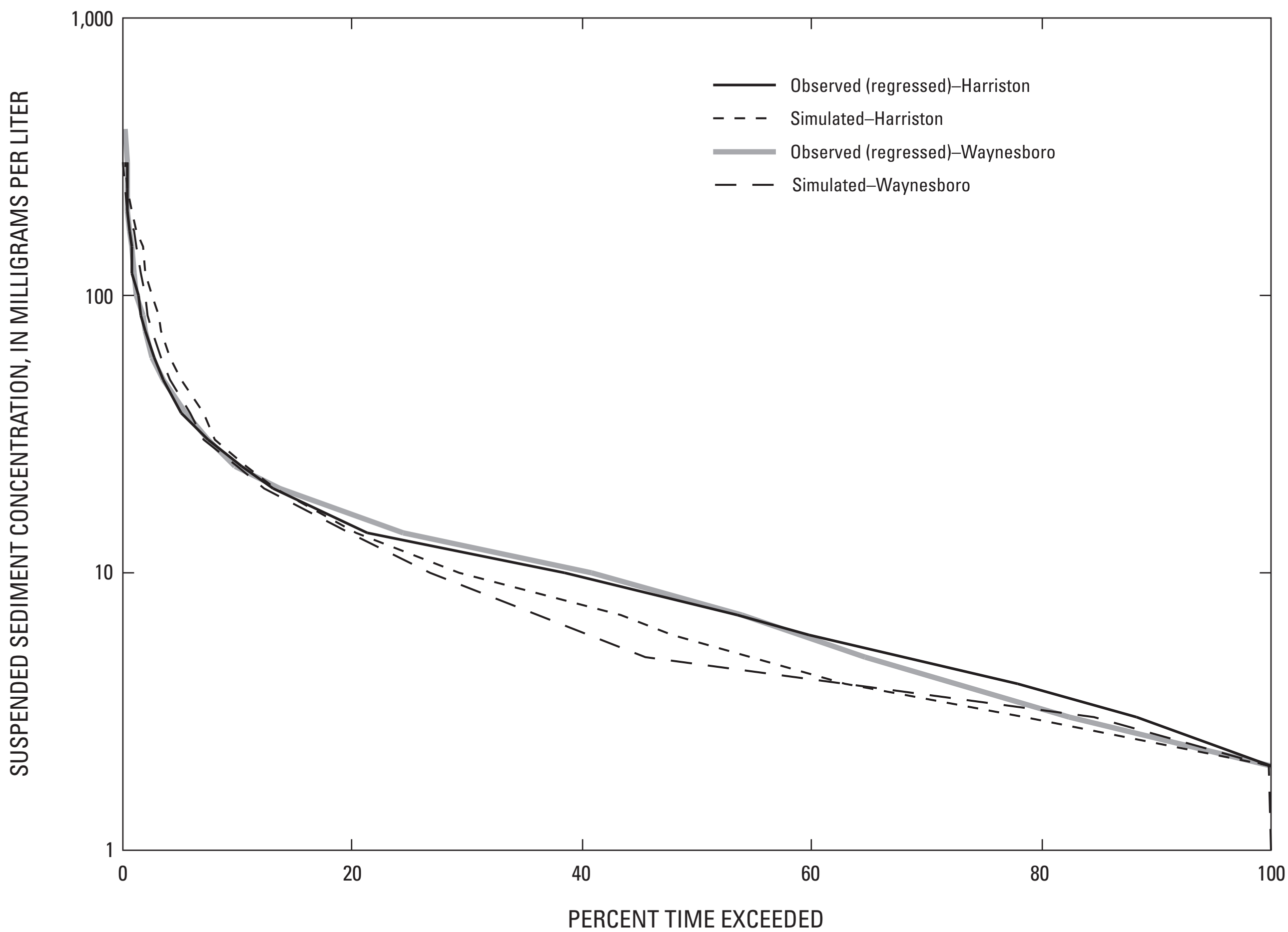



**Figure 46.** Duration plots for simulated and observed (regressed) daily suspended sediment concentration for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River, Virginia.

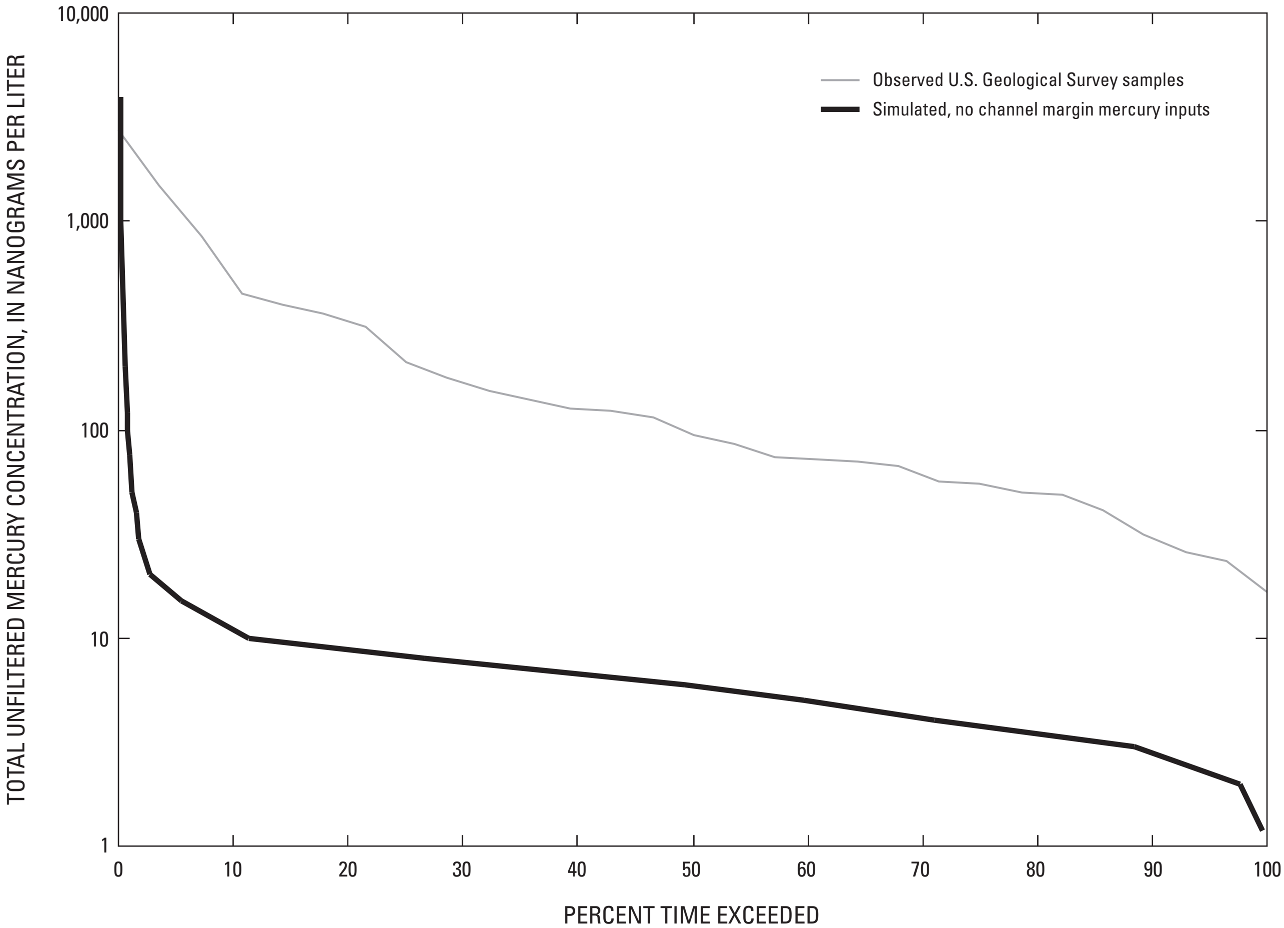



**Figure 47.** Simulated and observed (USGS samples only) total unfiltered mercury concentration distributions showing poor calibration obtained with no channel margin inputs, simulation period April 1, 2005, through March 31, 2007, South River at Dooms (USGS station number 01626920), Virginia.

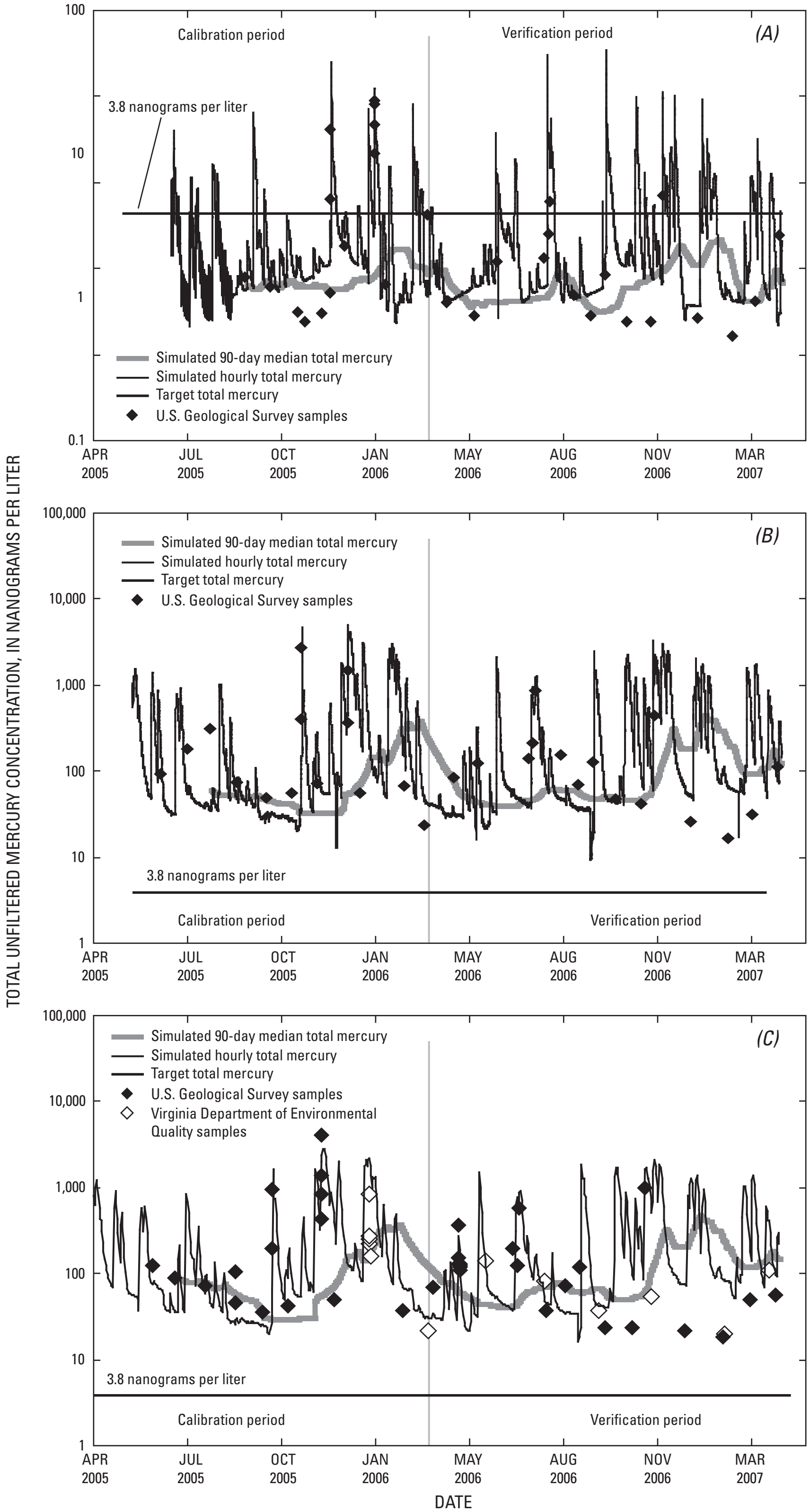



**Figure 48.** Simulated total unfiltered mercury concentration time series and observed concentrations, calibrated model, existing conditions, April 2005, through March 2007, *(A)* South River near Waynesboro (USGS station number 01626000), Virginia, *(B)* South River at Dooms, Virginia (USGS station number 01626920), Virginia, and *(C)* South River at Harriston (USGS station number 01627500), Virginia.

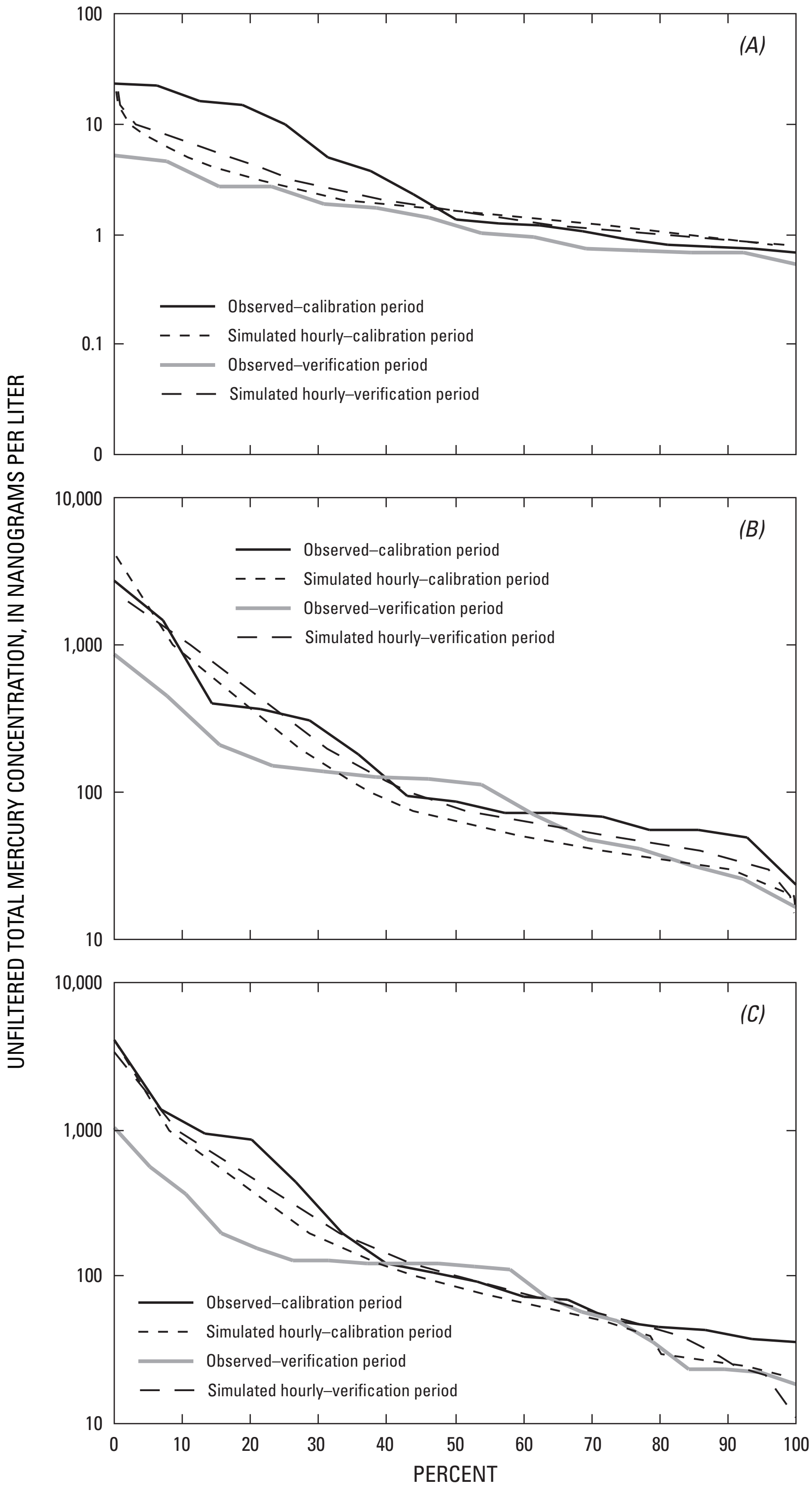



**Figure 49.** Duration curves for simulated and observed (USGS samples only) total unfiltered mercury concentrations, calibrated model, existing conditions, April 1, 2005, to March 31, 2007, South River *(A)* near Waynesboro, (USGS station number 01626000), Virginia, *(B)* at Dooms (USGS station number 0162920), Virginia, and *(C)* at Harriston (USGS station number 01627500), Virginia.

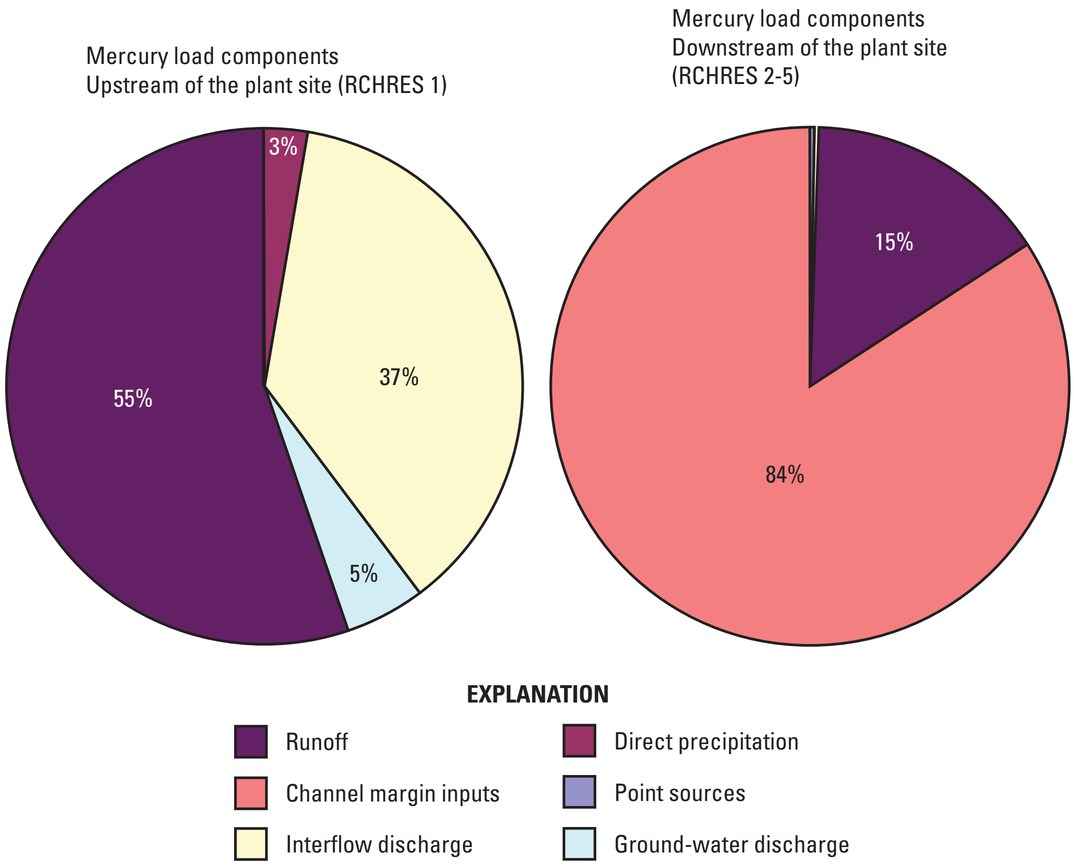



**Figure 50.** Percent mercury loading to the South River from sources upstream (model reach 1) and downstream (model reaches 2-5) of the plant site, calibrated model, existing conditions.

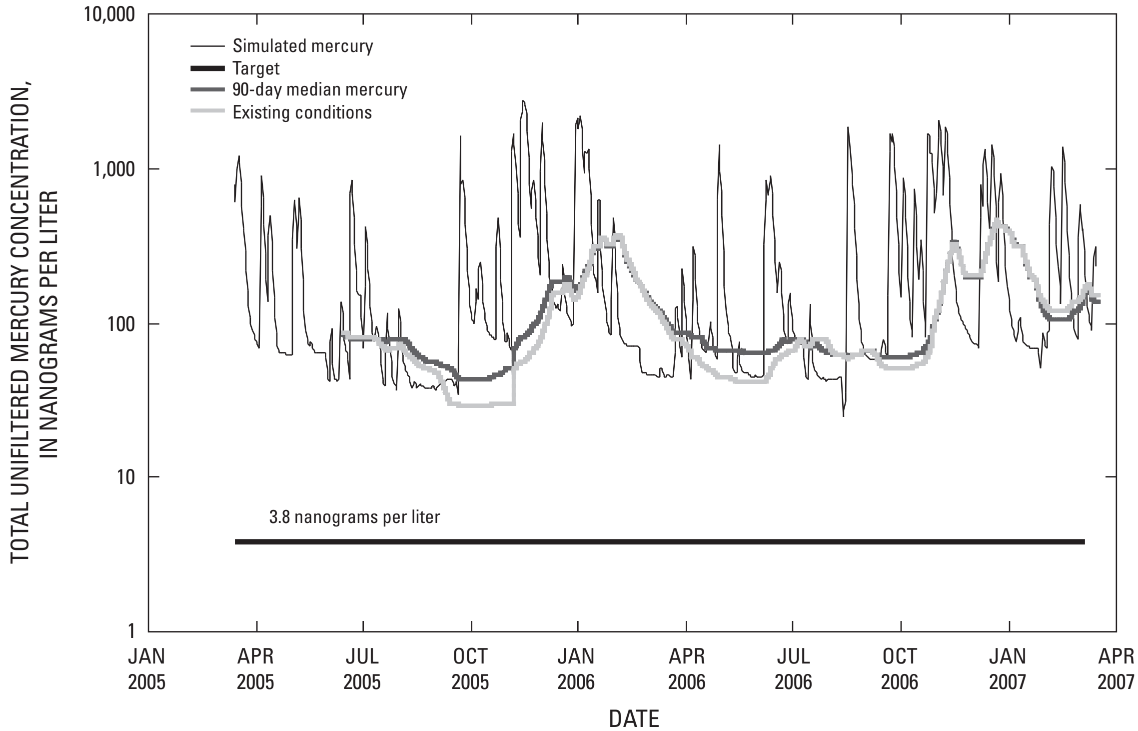



**Figure 51.** Simulated total unfiltered mercury values for the South River at Harriston (USGS station number 01627500), Virginia, under future conditions, scenario 2. [Existing 90-day median simulated mercury concentrations shown for comparison.]

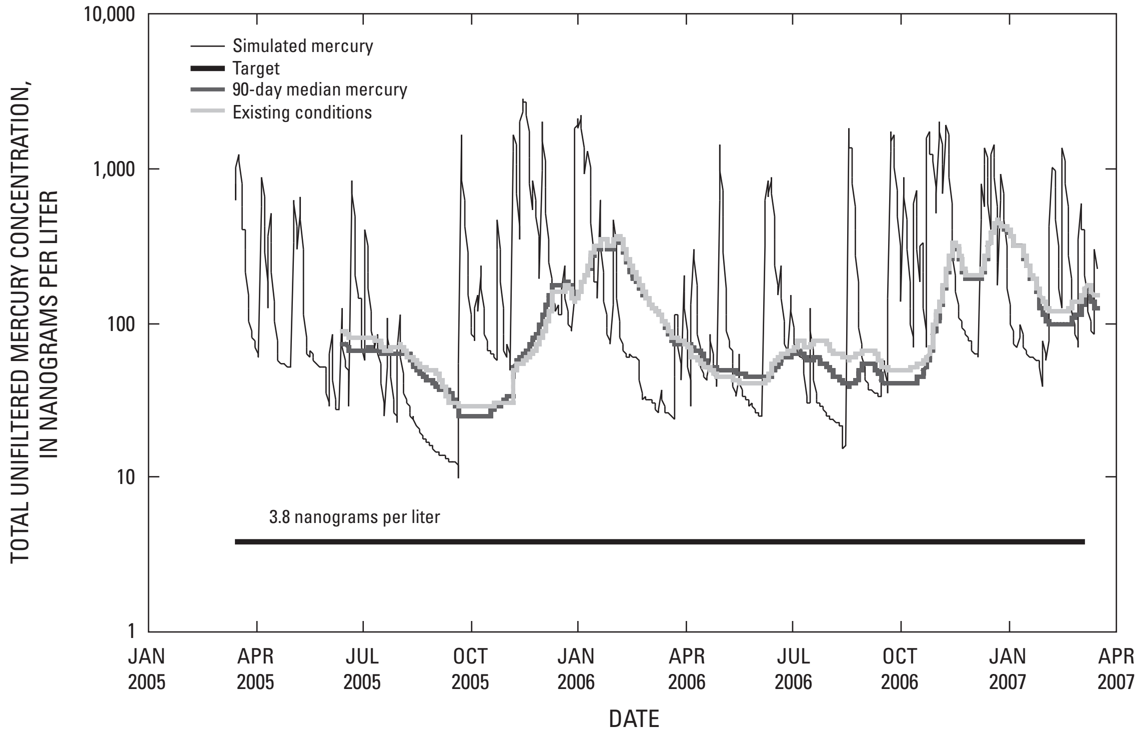



**Figure 52.** Simulated total unfiltered mercury values for the South River at Harriston (USGS station number 01627500), Virginia, under future conditions with point sources cleaned up, scenario 3A. [Existing 90-day median simulated mercury concentrations shown for comparison.]

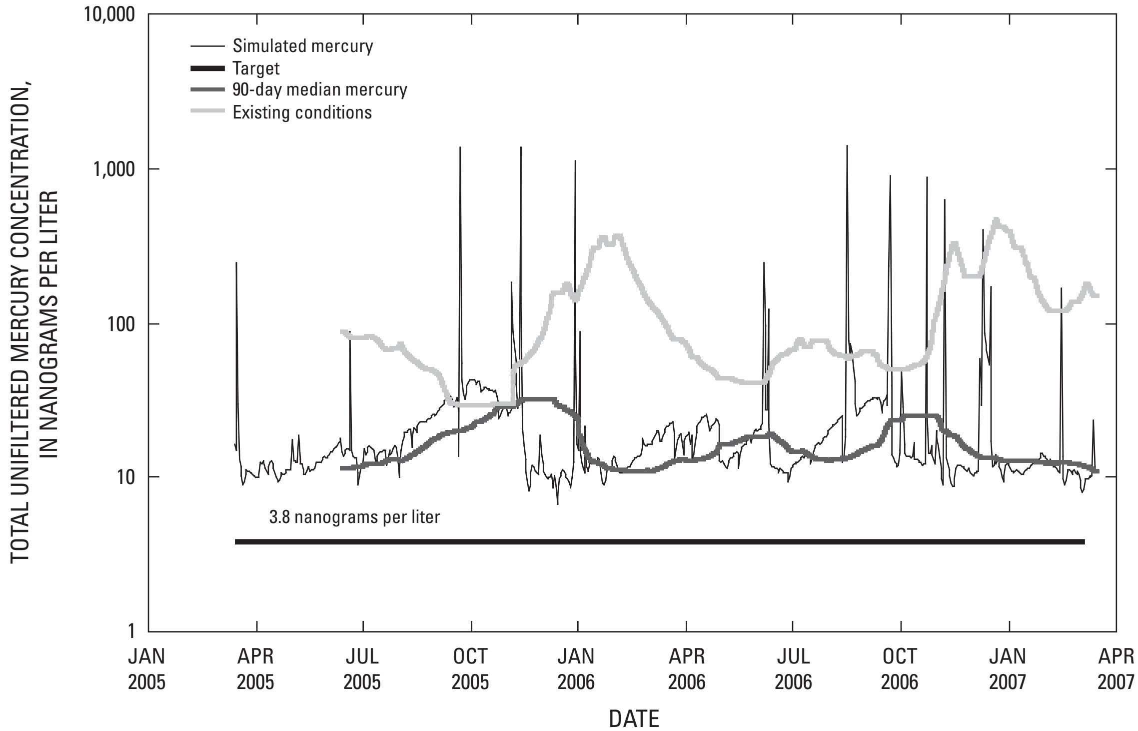



**Figure 53.** Simulated total unfiltered mercury values for the South River at Harriston (USGS station number 01627500), Virginia, under future conditions with channel margin mercury sources cleaned up, Scenario 3B. [Existing 90-day median simulated mercury concentrations shown for comparison.]

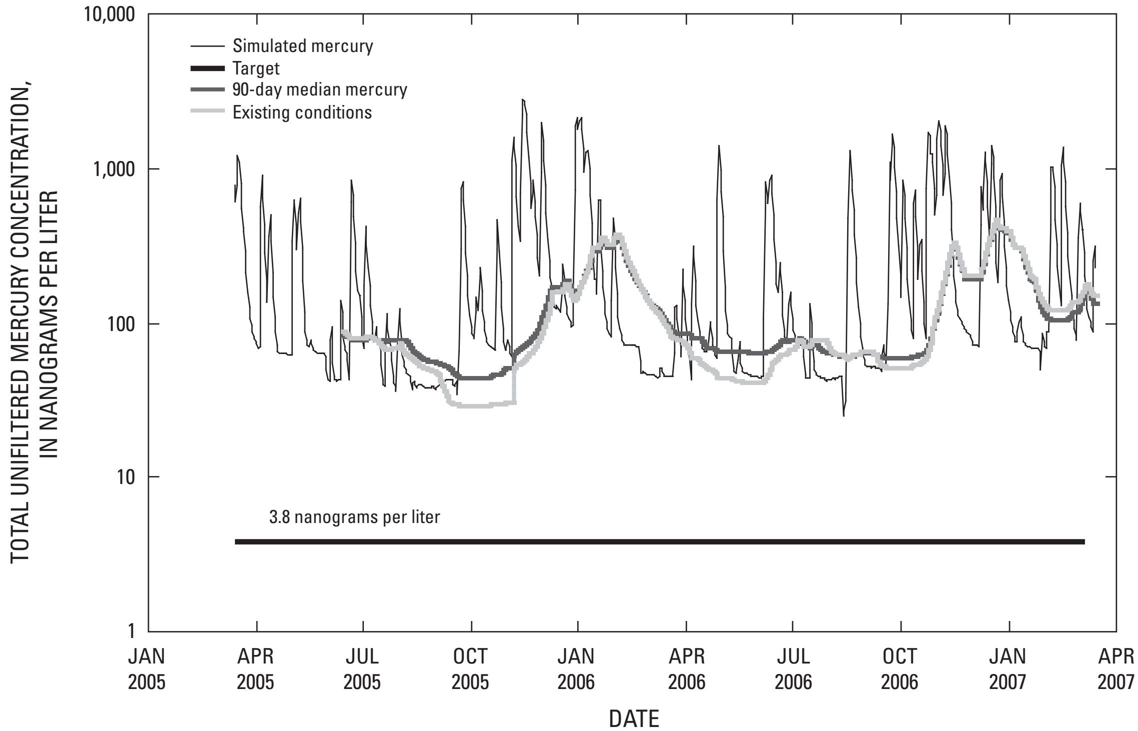



**Figure 54.** Simulated total unfiltered mercury values for the South River at Harriston (USGS station number 01627500), Virginia, under future conditions with runoff cleaned up, scenario 3C. [Existing 90-day median simulated mercury concentrations shown for comparison.]

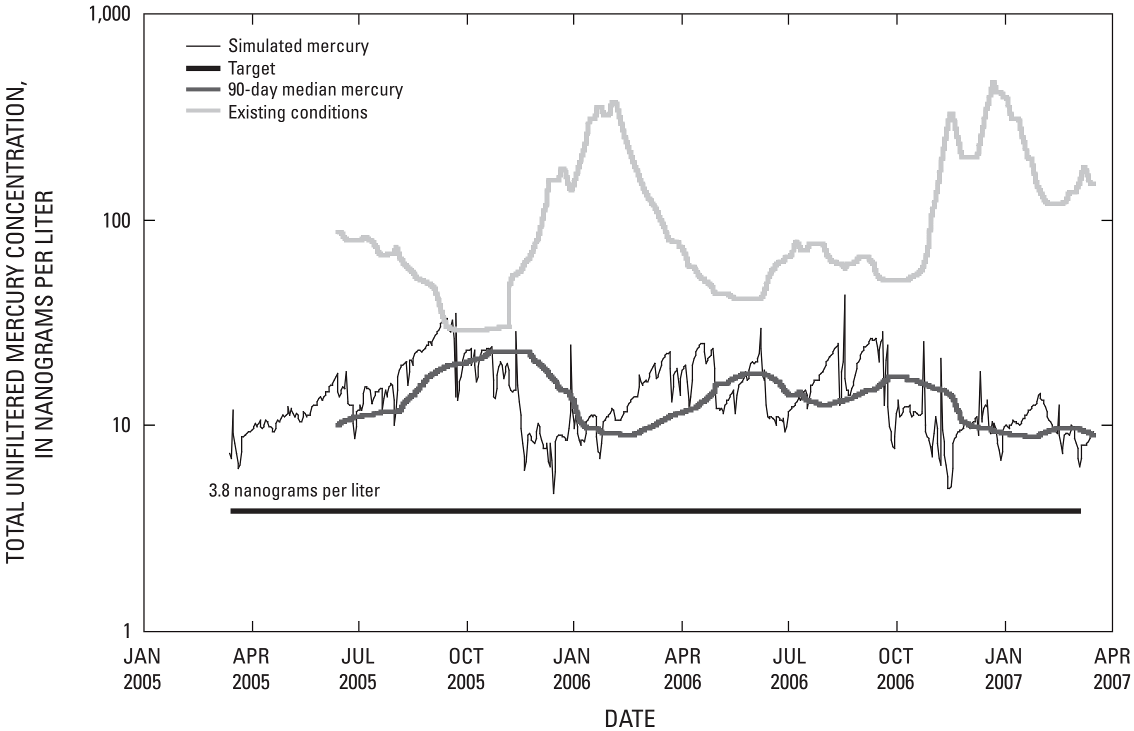



**Figure 55.** Simulated total unfiltered mercury concentrations for Scenario 4A, reduced channel margin and runoff mercury loads, South River at Harriston (USGS station number 01627500), Virginia. [Existing 90-day median simulated mercury concentrations shown for comparison.]

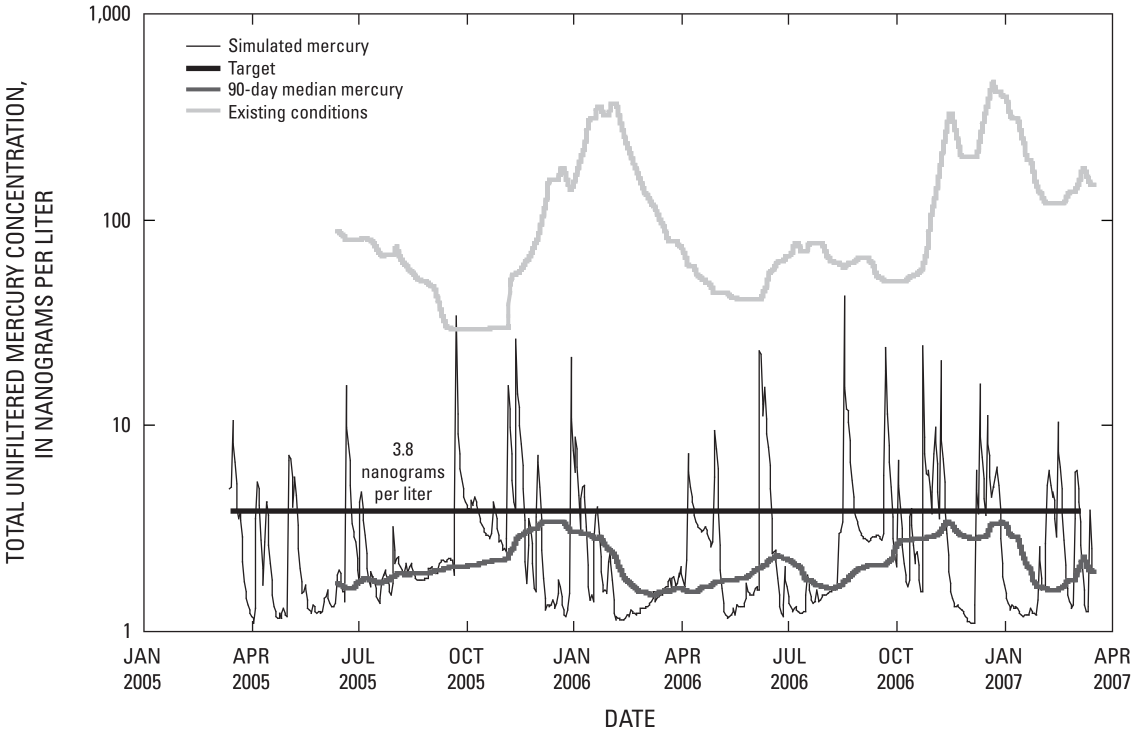



**Figure 56.** Simulated total unfiltered mercury concentrations for the Total Maximum Daily Load Scenario (Scenario 4B), reduced channel margin, runoff, and point-source mercury loads, South River at Harriston (USGS station number 01627500), Virginia. [Existing 90-day median simulated mercury concentrations shown for comparison.]

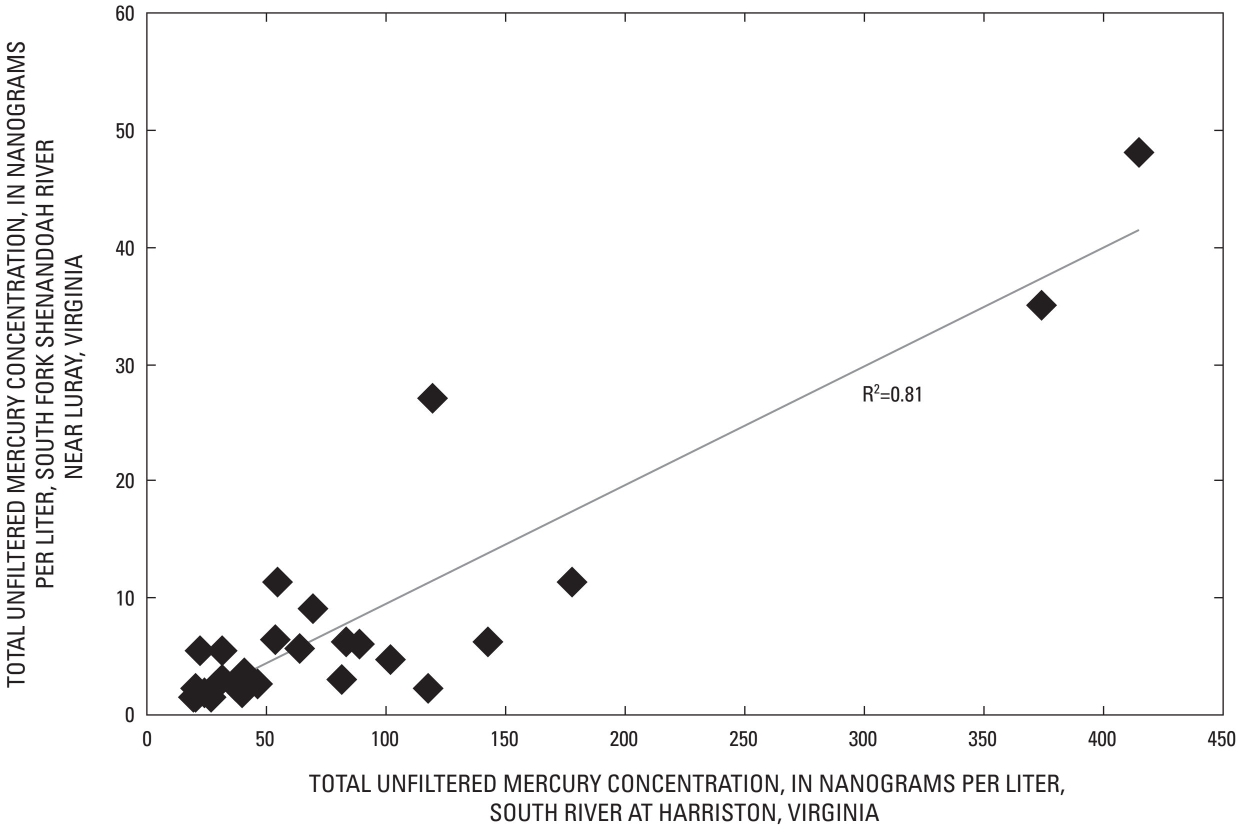



**Figure 57.** 1:1 Comparison of total unfiltered mercury concentrations (Virginia Department of Environmental Quality samples only) from the South River at Harriston (USGS station number 01627500) to same-day total unfiltered mercury concentrations from the South Fork Shenandoah River near Luray (USGS station number 01629500), Virginia.

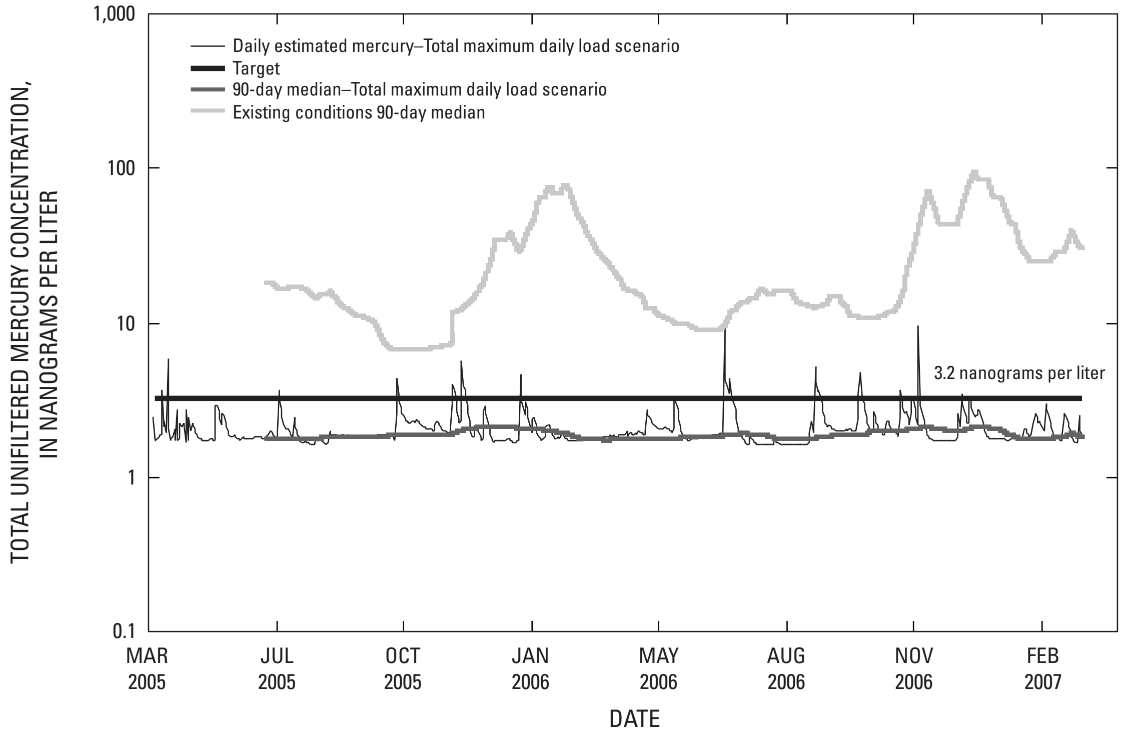



**Figure 58.** Simulated total unfiltered mercury concentrations for the Total Maximum Daily Load Scenario (Scenario 4B), reduced channel margin, runoff, and point-source mercury loads, South Fork Shenandoah River near Luray (USGS station number 01629500), Virginia. [Existing 90-day median simulated mercury concentrations shown for comparison.]

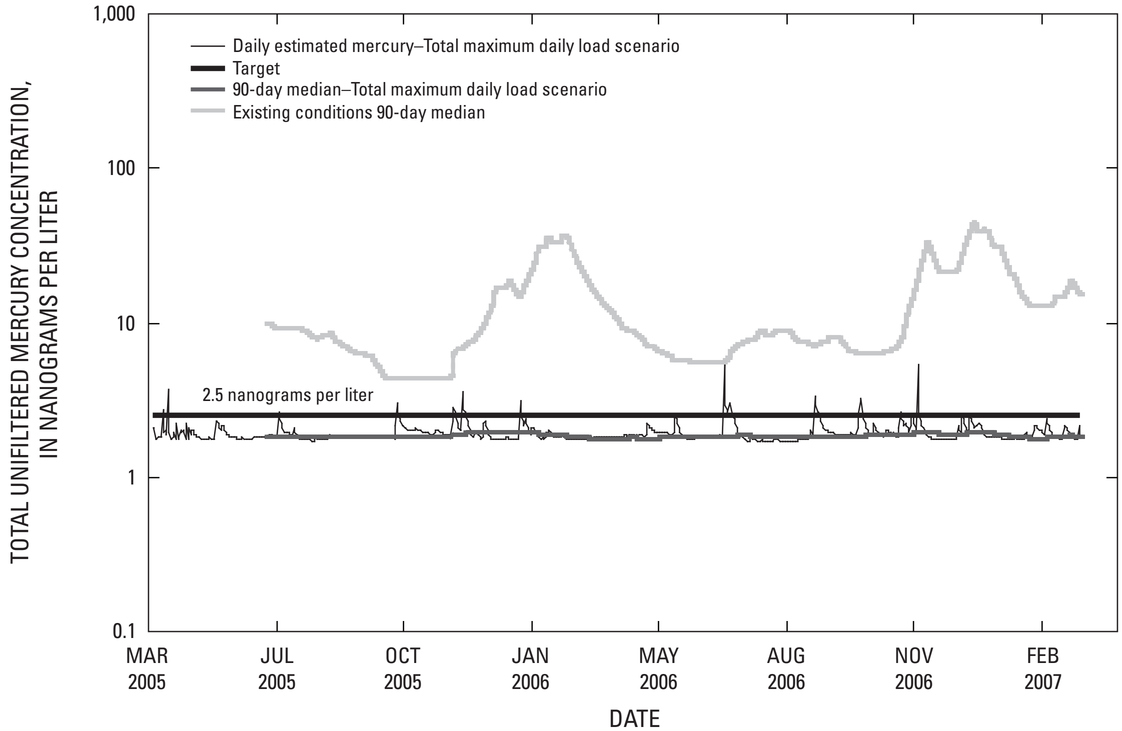



**Figure 59.** Estimated total unfiltered mercury concentrations for the Total Maximum Daily Load Scenario (Scenario 4B), reduced channel margin, runoff, and point-source mercury loads, Shenandoah River at the confluence with Craig Run, Clarke County, Virginia. [Existing 90-day median simulated mercury concentrations shown for comparison.]